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CONCEPT

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# with exclusive and brain storming MCQs

#### Practicing these MCQs help to strengthen your concepts and give you extra edge in your NEET preparation

- Of the following chemical equations:
  - $P + 3\text{LiAlH}_4 \longrightarrow X + 3\text{LiF} + 3\text{AlF}_3$

$$X + 6H_2O \longrightarrow Y + 6H_2$$

$$X + 3O_2 \xrightarrow{\Delta} B_2O_3 + 3H_2O$$

- P, X and Y respectively are
- (a)  $Na_2B_4O_7$ ,  $H_3BO_3$ ,  $B_2O_3$
- (b)  $H_3BO_3$ ,  $B_2H_6$ ,  $BF_3$
- (c)  $BF_3$ ,  $B_2H_6$ ,  $H_3BO_3$
- (d) H<sub>3</sub>BO<sub>3</sub>, Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>, B<sub>2</sub>O<sub>3</sub>
- A gas consist of 3 molecules with velocity 3 m/s, 5 molecules with velocity 8 m/s. The ratio of rms velocity and average velocity of the molecule is
  - (a) 1.75
- (b) 0.590 (c) 1.35
- (d) 1.078
- Oxidation numbers of each individual Br in Br<sub>3</sub>O<sub>8</sub> are
  - (a) 6, 4, 6
- (b) 4, 4, 4
- (c) 7, 5, 4
- none of these.
- At a certain temperature, the equilibrium constant  $(K_c)$  is 9/4 for the reaction :

$$CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)}$$

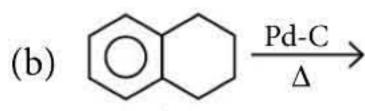
If we take 10 mole of each of the four gases in a one litre container, what would be the equilibrium mole per cent of  $H_{2(g)}$ ?

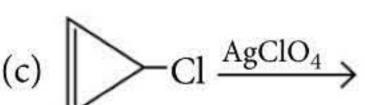
- (a) 30
- (b) 40
- (c) 35
- (d) 60

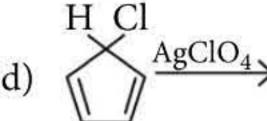
- A solution of (-)-1-chloro-1-phenylethane in toluene racemises slowly in the presence of a small amount of SbCl<sub>5</sub>, due to the formation of
  - (a) carbanion
- (b) carbene
- (c) carbocation
- (d) free radical.
- Select the correct order for bond angle.
  - (a)  $PH_3 < AsH_3 < NH_3 < SbH_3$
  - (b)  $F_2O < H_2O < Cl_2O$
  - (c)  $SbI_3 < SbBr_3 < SbCl_3$  (d)  $BF_3 > BCl_3 > BBr_3$
- In what ratio should you mix 0.2 M NaNO<sub>3</sub> and 0.1 M  $Ca(NO_3)_2$  solution so that in resulting solution, the concentration of -ve ion is 50% greater than concentration of +ve ion?
  - (a) 1:2
- (b) 2:1 (c) 3:1 (d) 3:2
- Which of the following reaction will not give an aromatic product?

(a) 
$$NaH \rightarrow$$

HH







- Which of the following statements are incorrect?
  - (1) All spectral lines belonging to Balmer series in hydrogen spectrum lie in visible region.

- (2) If a light of frequency υ falls on a metal surface having work function hv, photoelectric effect will take place only if  $\upsilon \le \upsilon_0$ .
- (3) The number of photoelectrons ejected from a metal surface in photoelectric effect depends upon the intensity of incident radiations.
- (4) The series limit wavelength of Balmer series for H-atoms is 4/R, where R is Rydberg's constant.
- (a) 1 and 2
- (b) 2 and 3
- (c) 1 and 4
- (d) 3 and 4
- 10. Which of the following is correct statement?
  - (a) Double chain silicates are known as amphiboles.
    - (b) In cyclic silicates two oxygen atoms per tetrahedron are shared.
    - (c) Orthosilicates contain discrete (SiO<sub>4</sub>)<sup>4-</sup> units.
    - (d) All of these.
- 11. Which of the following statements is not correct for the alkali metals?
  - (a) Their nitrates decompose on heating to give the corresponding nitrites and oxygen.
  - (b) Their chlorides are deliquescent and crystallises as hydrates.
  - (c) They react with water to form hydroxide and hydrogen.
  - (d) They readily react with halogens to form ionic halides,  $M^{\dagger}X^{-}$ .
- 12. Which is correct option for the properties specified?

  - (1) I < Br < Cl < F (Oxidising character)

  - (2) K > Mg > Al > B (Metallic character)

  - (3) C < O < N < F (Non-metallic character)
- (4) Li > Na > K > Rb > Cs (Chemical reactivity)
- (a) Only 1 and 2 (b) Only 2 and 3
- (c) Only 3 and 4 (d) Only 1 and 4
- 13. A 5.0 cm<sup>3</sup> solution of H<sub>2</sub>O<sub>2</sub> liberates 0.508 g of iodine from an acidified KI solution. Calculate the strength of  $H_2O_2$  solution in terms of volume strength at STP.
  - (a) 4.48 mL
- (b) 1.26 mL
- (c) 5.56 mL
- (d) 3.24 mL
- 14. In an oven, using 10 kg coal (assume the coal is 80% carbon in weight), insufficient oxygen is supplied such that 60% of carbon is converted to CO2 and 40% carbon is converted to CO. The heat generated, when coal is burnt in this fashion would be Given,  $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$ ;  $\Delta H = -394 \text{ kJ}$

$$C_{(s)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{(g)}; \Delta H = -111 \text{ kJ}$$

- (a) 183200 kJ
- (b) 187200 kJ
- (c) 185200 kJ
- (d) 181200 kJ.

- 15. Consider the following statements and select the correct option.
  - $S_1$ : Dust is the non-viable particulate.
  - $S_2$ : Particulates acquire negative charge and are attracted by the positive electrode.
  - $S_3$ :  $O_2$  is a greenhouse gas.
  - $S_4$ : Algae is a viable particulate.

  - (a) Only  $S_1$  and  $S_2$  (b) Only  $S_1$ ,  $S_2$  and  $S_3$

  - (c) Only  $S_1$ ,  $S_2$  and  $S_4$  (d) Only  $S_2$ ,  $S_3$  and  $S_4$

#### SOLUTIONS

- (c) :  $4BF_3 + 3LiAlH_4 \longrightarrow 2B_2H_6 + 3AlF_3 + 3LiF$  $B_2H_6 + 6H_2O \longrightarrow 2H_3BO_3 + 6H_2$   $(X) \qquad (Y)$   $B_2H_6 + 3O_2 \xrightarrow{\Delta} B_2O_3 + 3H_2O$ 
  - (d):  $u_{av} = \frac{n_1 v_1 + n_2 v_2}{n_1 + n_2 v_2}$  $u_{av} = \frac{3 \times 3 + 5 \times 8}{3 + 5} = \frac{49}{8} = 6.125$  $u_{rms} = \sqrt{\frac{n_1 v_1^2 + n_2 v_2^2}{n_1 + n_2}}$  $= \sqrt{\frac{(3\times9) + (5\times64)}{8}} = \frac{18.628}{2.82} = 6.605$  $\frac{u_{rms}}{u_{av}} = \frac{6.605}{6.125} = 1.078$
- Tribromooctaoxide
- $CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)}$ 10 10 10 (a): Initial moles Moles at eq. (10-x) (10-x) (10+x) (10+x)Where, x is the number of moles of each reactant changed to the products at equilibrium.

$$K = \frac{(10+x)^2}{(10-x)^2} = 9/4 \text{ (given)}; \frac{10+x}{10-x} = 3/2 \Rightarrow x = 2$$

Mole % of 
$$H_{2(g)}$$
 at eq. =  $\frac{10+x}{40} \times 100 = 30\%$ 

5. (c) : 
$$Cl-CH-CH_3 \xrightarrow{SbCl_5} \xrightarrow{Toluene}$$
  
Ph
(-)

$$Ph-CH_{3} + SbCl_{6}^{-} \longrightarrow Ph-CH-CH_{3} + SbCl_{5}$$
(Carbocation)
$$Cl$$
(± dl-mixture)

- 6. (b): (a)  $NH_3 > PH_3 > AsH_3 > SbH_3 Bond angle$ 
  - (b)  $Cl_2O > H_2O > F_2O$
  - (c)  $SbI_3 > SbBr_3 > SbCl_3$
  - (d) All are trigonal planar (bond angle 120°).
- 7. (a): Suppose  $V_1$  mL of NaNO<sub>3</sub> is mixed with  $V_2$  mL of Ca(NO<sub>3</sub>)<sub>2</sub>

mM of NaNO<sub>3</sub> mixed =  $0.2 \times V_1$ 

mM of  $Ca(NO_3)_2$  mixed =  $0.1 \times V_2$  (because mole ratio of  $Ca^{2+}$ :  $NO_3^-$  in  $Ca(NO_3)_2$  is 1:2)

: Molarity of  $NO_3^-$  in mixture =  $[NO_3^-]$  of  $NaNO_3 + [NO_3^-]$  of  $Ca(NO_3)_2$ 

$$\frac{0.2 \times V_1}{(V_1 + V_2)} + \frac{0.1 \times 2 \times V_2}{(V_1 + V_2)} = \frac{0.2 \times V_1 + 0.2 \times V_2}{(V_1 + V_2)}$$

Molarity of Na<sup>+</sup> and Ca<sup>2+</sup> ions in mixture

$$= \frac{0.2 \times V_1}{(V_1 + V_2)} + \frac{0.1 \times V_2}{(V_1 + V_2)} = \frac{0.2 V_1 \times 0.1 V_2}{(V_1 + V_2)}$$

$$= \frac{3}{2} \left[ \frac{0.2V_1 + 0.1V_2}{(V_1 + V_2)} \right] \Rightarrow \frac{V_1}{V_2} = \frac{1}{2}$$

8. (d):  $\stackrel{\text{H Cl}}{\swarrow} \stackrel{\text{AgClO}_4}{\longrightarrow}$  After removal of Cl-atom,

The intermediate formed is anti-aromatic, so this reaction is not possible.

- 9. (a): (1) Only first four spectral lines belonging to Balmer series in hydrogen spectrum lie in visible region.
  - (2) If a light of frequency v, falls on a metal surface, having work function hv, photoelectric effect will take place only if  $v \ge v_0$ , since  $v_0$  is the minimum frequency required for photoelectric effect.
- 10. (d): (1) The double chain silicates can be drawn in which two simple chains are joined together by shared oxygen. Such compounds are also known as amphiboles.
  - (2) If two oxygen atoms per tetrahedron are shared to form closed rings such that the structure with general formula  $(SiO_3^{2-})_n$ , or  $(SiO_3)_n^{2n-}$  is obtained, the silicates containing these anions are called cyclic silicates.
  - (3) Orthosilicates contain discrete  $(SiO_4)^{4-}$  units. *i.e.*, there is no sharing of corners with one another.
- 11. (b): Only LiCl is deliquescent and crystallise, as a hydrate LiCl.2H<sub>2</sub>O.
- **12.** (a): (3) C < N < O < F (Non-metallic character)
  - (4) Correct order is Li < Na < K < Rb < Cs.

For metals chemical reactivity increases down the group with decreasing ionisation energy.

- 13. (a):  $H_2O_2 + H_2SO_4 + 2Kl \longrightarrow I_2 + K_2SO_4 + 2H_2O_3$ 34 g 254 g
  - $\therefore$  254 g of I<sub>2</sub> is produced by 34 g of H<sub>2</sub>O<sub>2</sub>
  - $\therefore 0.508 \text{ g of I}_2 \text{ will be produced by } \frac{34}{254} \times 0.508 \text{ g}$  $= 0.068 \text{ g H}_2\text{O}_2$

Hence, 5 mL of  $H_2O_2$  solution contains = 0.068 g  $H_2O_2$ 

∴ 1 mL of H<sub>2</sub>O<sub>2</sub> solutions will contain

$$=\frac{0.068}{5}$$
g H<sub>2</sub>O<sub>2</sub>

 $2H_2O_2 \longrightarrow 2H_2O + O_2$ 68 g 22.4 L at STP

 $68 \text{ g of H}_2\text{O}_2 \text{ produces} = 22.4 \text{ L O}_2 \text{ at STP}$ 

or 1 mL (*i.e.*,  $\frac{0.068}{5}$  g) of H<sub>2</sub>O<sub>2</sub> produces

$$= \frac{22400}{68} \times \frac{0.068}{5} = 4.48 \,\text{mL O}_2 \,\text{at STP}$$

i.e., the volume strength of  $H_2O_2$  solution is 4.48. ("Volume strength" indicates the mL of  $O_2$  at STP obtained from 1 mL of  $H_2O_2$  solution.)

14. (b): As coal has 80% carbon in weight weight of carbon in 10 kg coal

$$=10 \times \frac{80}{100} = 8 \text{ kg} = 8000 \text{ g}$$

As 60% of C is converted to CO<sub>2</sub> thus wt. of C converted into CO<sub>2</sub>

$$=8000 \times \frac{60}{100} = 4800 \text{ g}$$

and 40% of C to CO thus wt. of C converted into

$$CO = 8000 \times \frac{40}{100} \times = 3200 \text{ g}$$

Now from eq. (i) 12 g (1 mole) of C on combustion liberates = 394 kJ of heat

∴ 4800 g of C on combustion liberates

$$= \frac{394 \times 4800}{12} \text{ kJ} = 157600 \text{ kJ} \qquad \dots (i)$$

From eq. (ii) 12 g (1 mole) of C on combustion liberates = 111 kJ of heat

∴ 3200 g of C on combustion liberates

$$=\frac{111\times3200}{12}$$
 kJ = 29600 kJ

Total heat liberated would be = 157600 + 29600= 187200 kJ

15. (c)





# NEET/JEE

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2020

Unit 2

# Classification of Elements and Periodicity in Properties | Chemical Bonding and Molecular Structure

# Classification of Elements and Periodicity in Properties

#### GENESIS OF PERIODIC CLASSIFICATION

- Dobereiner's Triads: The element in a triad has similar properties and the atomic weight of the middle element of each triad is very close to the arithmetic mean of atomic weight of the other two elements.
- De Chancourtois Classification: The elements were arranged in order of increasing atomic weights and a cylindrical table of elements was proposed to display the periodic recurrence of properties.
- Newland's Law of Octaves: When the elements are arranged in the increasing order of atomic weights, the properties of every eighth element were similar to the first one like the eighth note of a musical scale.
- Lothar Meyer's Arrangements: When the properties of the elements such as atomic volume, m.pt., b.pt., etc., are plotted as a function of their atomic weights, the elements with similar properties occupied almost similar positions on the curve.

#### MENDELEEV'S PERIODIC TABLE

- The physical and chemical properties of elements are a periodic function of their atomic weights.
- Characteristics of Mendeleev's Periodic Table :
  - (i) Eight vertical columns, called groups.
  - (ii) Six horizontal rows, called periods.

- Significance of Mendeleev's Periodic Table :
  - Instead of studying properties of elements separately, they can be studied in groups containing elements with same properties.
  - At his time only 63 elements were known. He left blank spaces or gap for unknown elements.
  - Mendeleev's periodic table corrected the doubtful atomic weights.

#### Modern Periodic Table

- According to Moseley "physical and chemical properties of elements are the periodic functions of their atomic numbers".
- Cause of Periodicity: The cause of periodicity in properties is the repetition of similar outer electronic configurations after certain regular intervals.
- Long form of periodic table consists of seven horizontal rows called 'periods' and eighteen vertical columns called 'groups'.
- There are some common names given to few groups also:
  - Elements of group-1 are called alkali metals.
  - Elements of group-2 are called alkaline earth metals.

- Elements of group-11 are called coinage metals.
- Elements of group-15 are called pnictogens.
- Elements of group-16 are called chalcogens.
- Elements of group-17 are called halogens.
- Elements of group-18 are called noble gases or inert gases.
- IUPAC Nomenclature of Elements with Atomic Number 100: The name of an element is derived directly from its atomic number using the numerical root for 0 to 9. These roots are tabulated below.

#### Notation for IUPAC nomenclature of elements

Digit	Name	Abbreviation	
0	nil	n	
1	un	u	
2	bi	b	
3	tri	t	
4	quad	q	
5	pent	p	
6	hex	h	
7	sept	s	
8	oct	О	
9	enn	e	

# ELECTRONIC CONFIGURATIONS AND TYPES OF ELEMENTS

- **s-Block Elements**: Elements in which the last electron enters the s-orbital of their respective outermost shells are called s-block elements. General outer shell electronic configuration of s-block elements is  $ns^{1-2}$ , where, n = 2-7.
- **p-Block Elements**: Elements in which the last electron enters any one of the three *p*-orbitals of their respective outermost shells are called *p-block elements*. General outer shell electronic configuration of *p*-block elements is  $ns^2np^{1-6}$ , where n = 2-7.
- **d-Block Elements**: Elements in which the last electron enters any one of the five *d*-orbitals of their respective penultimate shells are called *d-block elements*. General outer shell electronic configuration of *d*-block elements is  $(n-1)d^{1-10}ns^{0-2}$ , where n = 4-7.
- f-Block Elements: Elements in which the last electron enters any one of the seven f-orbitals of their respective anti-penultimate shells are called

*f-block elements*. General outer shell electronic configuration of *f*-block elements is  $(n-2)f^{1-14}$   $(n-1)d^{0-1}ns^2$ , where n = 6-7.

# PEEP INTO PREVIOUS YEARS

- 1. The element with Z = 120 (not yet discovered) will be an/a
  - (a) inner-transition metal
  - (b) alkaline earth metal
  - (c) alkali metal
  - (d) transition metal.

(JEE Main 2019)

- 2. The element Z = 114 has been discovered recently. It will belong to which of the following family/group and electronic configuration?
  - (a) Carbon family, [Rn]  $5f^{14} 6d^{10} 7s^2 7p^2$
  - (b) Oxygen family, [Rn]  $5f^{14} 6d^{10} 7s^2 7p^4$
  - (c) Nitrogen family, [Rn]  $5f^{14} 6d^{10} 7s^2 7p^6$
  - (d) Halogen family, [Rn]  $5f^{14} 6d^{10} 7s^2 7p^5$

(NEET 2017)

- 3. An element *X* belongs to fourth period and fifteenth group of the periodic table. Which of the following statements is true?
  - (a) It has a completely filled *s*-orbital and a partially filled *d*-orbital.
  - (b) It has completely filled *s*-and *p*-orbitals and a partially filled *d*-orbital.
  - (c) It has completely filled *s*-and *p*-orbitals and a half-filled *d*-orbital.
  - (d) It has a half-filled *p*-orbital and completely filled *s*-and *d*-orbitals. (WB JEE 2016)

#### Periodic Trends in Properties of Elements

- Atomic Radii: Distance from the centre of the nucleus to the outermost shell of electrons. Types of atomic radii:
  - Covalent radius: One half of the distance between the centre of nuclei of two similar atoms bonded by a single covalent bond.
  - Metallic radius: One half of the internuclear distance between the two neighbouring atoms of a metal in the metallic lattice.
  - van der Waals' radius: van der Waals' radius is one half of the distance between nuclei of two identical non-bonded isolated atoms. Noble gases held by weak van der Waals' forces of attraction.
- Variation of Atomic Radii in the Periodic Table
  - Variation in a period: The atomic radii ↓ with
     ↑ in atomic number on going from left to right due to the increase of effective nuclear charge.

- Variation in a group: The atomic radii of elements ↑ from top to bottom in a group. On moving down a group, the effective nuclear charge ↓ with ↑ in atomic number.
- **Ionic Radii**: The effective distance from the centre of the nucleus of the ion up to which it exerts its influence on its electronic cloud.
  - The ionic radii share the same trends as atomic radius.
  - The radius of positive ion (cation) is always smaller than that of the parent atom because it has lesser electrons but same nuclear charge.
  - The radius of negative ion (anion) is larger than that of the parent atom because extra electrons are added due to which repulsion among electrons increases and effective nuclear charge decrease.
- **Isoelectronic Species**: Atoms or ions having the same number of electrons but different magnitude of nuclear charge. *e.g.*, O<sup>2-</sup>, F<sup>-</sup>, Na<sup>+</sup> and Mg<sup>2+</sup> have 10 electrons.
- Ionisation Enthalpy: It is the energy required to remove an electron from an isolated gaseous atom in its ground state.

$$M_{(g)} + I.E. \longrightarrow M^+_{(g)} + e^-$$

- If gaseous atom is to lose more than one electrons, they can be removed only one after another *i.e.*, in succession and not simultaneously. This is known as *successive* ionisation energy or potential:

$$I.E_3 > I.E_2 > I.E_1$$

- The screening effect or shielding effect: In a multielectron atom, valence shell electrons experience less attractive force from the nucleus due to repulsion between inner shell electrons and valence electrons. This is called screening effect or shielding effect.
- Factors affecting ionisation enthalpy:
  - Size of atom :  $I.E. \propto \frac{1}{\text{Size of atom}}$
  - ➤ Nuclear charge : I.E. ∞ Nuclear charge
  - Screening effect :  $I.E. \propto \frac{1}{\text{Screening effect}}$
  - Completely filled or half-filled orbitals: It is comparatively difficult to remove the electrons from these orbitals (being more stable).

- **Type of electrons involved :** Ionisation energy decreases in the order of s > p > d > f-orbitals.
- Ionisation energy decreases down the group due to increase in size of the atom and screening effect of intervening electrons.
- Electron Gain Enthalpy: It may be defined as the amount of energy released when an electron is added to an isolated gaseous atom of the element.

$$A_{(g)} + e^{-} \longrightarrow A_{(g)}^{-}; \Delta_{eg}H$$

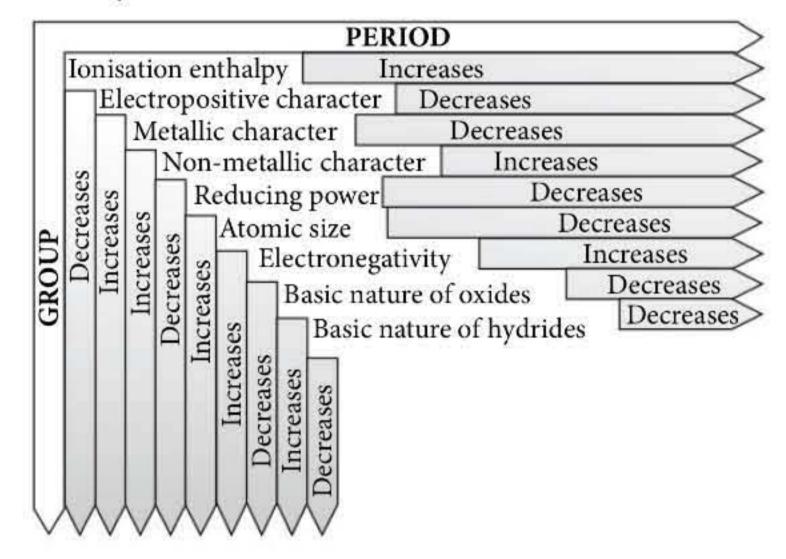
- Factors affecting electron gain enthalpy:
  - Size of the atom :  $\Delta_{eg}H \propto \frac{1}{\text{Size of atom}}$
  - Nuclear charge :  $\Delta_{eg}H \propto \text{Effective nuclear charge}$
  - Screening effect :  $\Delta_{eg}H \propto \frac{1}{\text{Screening effect}}$
- Electron gain enthalpy becomes less negative as we move down a group.
- Electron gain enthalpy becomes more and more negative from left to right in a period (except for noble gases).
- Electronegativity: It is the tendency of an atom to attract the shared pair of electrons towards itself in a covalent bond. Greater the electronegativity of an atom, greater will be its tendency to attract the shared pair of electrons towards itself.
  - Electronegativity decreases on moving down the group and increases along a period.

#### **Periodic Trends in Chemical Properties**

- As we have seen, the ionization enthalpy of the extreme left element in a period is the least and the electron gain enthalpy of the element on the extreme right is the highest negative (excluding noble gases). This results in high chemical reactivity at the two extremes and the lowest in the centre.
- Thus, alkali metals (at extreme left) has maximum tendency to form cation (by loss of an electron) and halogens (at extreme right) has maximum tendency to form anion (by gain of an electron).
- Thus, metallic character is maximum at the left and non-metallic character is maximum at the right within a period.
- The oxides formed by the elements at the left of the periodic table are basic (e.g., Na<sub>2</sub>O) while oxides formed by the elements at the right of the periodic

- table are acidic (e.g.,  $CL_2O_7$ ). However, oxides of elements in the centre are either amphoteric (e.g.,  $Al_2O_3$ ,  $As_2O_3$ ) or neutral (e.g., CO, NO,  $N_2O$ ).
- In transition metals, change in atomic radii is much smaller than representative elements (*p*-block elements). Their ionization enthalpies are between *s*-and *p*-block elements. Therefore, they are less electropositive than group 1 and 2 metals.

#### **Summary of Some General Trends:**



# PEEP INTO PREVIOUS YEARS

- 4. For the second period elements the correct increasing order of first ionization enthalpy is
  - (a) Li < Be < B < C < O < N < F < Ne
  - (b) Li < Be < B < C < N < O < F < Ne
  - (c) Li < B < Be < C < O < N < F < Ne
  - (d) Li < B < Be < C < N < O < F < Ne

(NEET 2019)

- 5. The correct order of atomic radii in group 13 elements is
  - (a) B < Al < In < Ga < Tl
  - (b) B < Al < Ga < In < Tl
  - (c) B < Ga < Al < Tl < In
  - (d) B < Ga < Al < In < Tl

(NEET 2018)

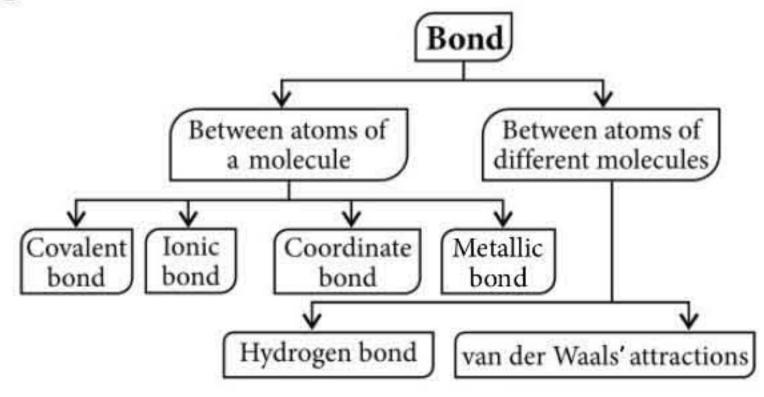
- 6. The option(s) with only amphoteric oxides is (are)
  - (a)  $Cr_2O_3$ , BeO, SnO, SnO<sub>2</sub>
  - (b) ZnO, Al<sub>2</sub>O<sub>3</sub>, PbO, PbO<sub>2</sub>
  - (c) NO, B<sub>2</sub>O<sub>3</sub>, PbO, SnO<sub>2</sub>
  - (d) Cr<sub>2</sub>O<sub>3</sub>, CrO, SnO, PbO (JEE Advanced 2017)

# Chemical Bonding and Molecular Structure

# CHEMICAL BOND

 The attractive force which holds together the constituent particles (atoms, ions or molecules) in a chemical species is known as chemical bond.

#### Types of Bonds:



- Covalent Bond: The bond which is formed between two combining atoms by the mutual sharing of electron pair(s) is called *covalent bond*. The compounds containing a covalent bond are called *covalent compounds*.
- **Ionic or Electrovalent Bond :** Ionic bond is a type of chemical bond that involves the electrostatic force of attraction between oppositely charged ions together, is known as *ionic bond* and *electrovalent bond*.

- Octet Rule: The principle of attaining maximum of eight electrons in the valence shell of atom is called octet rule. The octet rule is violated in a significant number of cases:
  - The octet rule does not work in case of atoms which have less than four outer electrons, even if all the outer electrons are used to form bond, an octet cannot be attained.
  - The octet rule does not work in case of atoms which have an extra energy level that may accept electrons and can be used for bonding. For example, PF<sub>3</sub> obeys the octet rule, but PF<sub>5</sub> does not.
  - The octet rule does not work in molecules which have an odd number of electrons, such as NO and ClO<sub>2</sub>, nor does it explain why O<sub>2</sub> is paramagnetic and has two unpaired electrons.
- Formal Charge: The formal charge of an atom in a polyatomic molecule or ion may be defined as the difference between the number of valence electrons of that atom in an isolated or free state and the number of electrons assigned to the atom in the Lewis structure.
  - Formal charge = Total no. of valence electrons in the free atom Total no. of electrons of lone pairs (non-bonding electrons)  $-\frac{1}{2} \times$  total no. of shared electrons (bonding electrons).

# PEEP INTO PREVIOUS YEARS

7. Which of the following is the correct electron dot structure of N<sub>2</sub>O molecule?

(a) 
$$: \ddot{N} = N = \ddot{\ddot{O}}$$

(b) 
$$: \ddot{\mathbf{N}} - \mathbf{N} = \ddot{\mathbf{O}}$$
:

(a) 
$$: \ddot{N} = N = \ddot{O}$$
 (b)  $: \ddot{N} - N = \ddot{O}$ :  
(c)  $: N = N = \ddot{O}$ : (d)  $: N \equiv \overset{+}{N} - \ddot{O}$ :

$$(d): N \equiv \overset{+}{N} - \ddot{O}$$

#### (Karnataka CET 2017)

- **8.** The correct statement for the molecule, CsI<sub>3</sub>, is
  - (a) it contains Cs<sup>+</sup>, I<sup>-</sup> and lattice I<sub>2</sub> molecule
  - (b) it is a covalent molecule
  - (c) it contains  $Cs^+$  and  $I_3^-$  ions
  - (d) it contains Cs<sup>3+</sup> and I<sup>-</sup> ions. (JEE Main 2014)

#### BOND PARAMETERS

The various characteristics features shown by a bond are called the bond parameters

Bond Length: "The average distance between the centres of the nuclei of two bonded atoms in a molecule.

Covalent radius = 
$$r_A + r_B = \frac{d}{2}$$
 [if  $r_A = r_B$ ]

- **Bond Enthalpy:** The amount of energy (in kJ mol<sup>-1</sup>) required to break one mole of bond of a particular type between two atoms to separate them in gaseous state.
- Bond Angle: The angle between the lines representing the directions of the bond. *i.e.*, orbital containing the bonding electrons is called bond angle.
- **Bond Order**: The bond order is given by the number of bonds between the two atoms in a molecule. e.g., Bond order in  $H_2$  is one, in  $O_2$  it is two and in  $N_2$  it is three.
  - Isoelectronic molecules and ions have identical bond order. For example  $F_2$  and  $O_2^{2-}$  have bond order 1 and N<sub>2</sub>, CO and NO<sup>+</sup> have bond order 3.
  - The stabilities of molecules can be understood by the statement "With increase in bond order, bond enthalpy increases and bond length decrease."

#### **Polarity of Bond:**

Dipole moment ( $\mu$ ) = Charge (q) × Distance of separation (d)

It is usually expressed in Debye (D).

SI unit of dipole moment is Cm.  $1 D = 3.335 \times 10^{-30} Cm$ .

Percent ionic character

% ionic character can also be calculated by using,

Pauling equation = 
$$18(\chi_A - \chi_B)^{1.4}$$

$$= 16(\chi_A - \chi_B) + 3.5(\chi_A - \chi_B)^2$$

Fajan's Rule: The power of an ion (cation) to distort the electronic cloud of other ion (anion) is known as its polarising or polarisation power, whereas the tendency of an ion (anion) to get polarised by other ion is known as its *polarisability*. Higher the degree of ionic polarisation greater is the covalent character.

- Polarising power 
$$\propto \frac{1}{\text{size of cation}}$$

- Polarisability of anion ∞ size of anion
- Covalent character ∞ size of anion

$$\propto \frac{1}{\text{size of cation}} \propto \text{charge on anion and cation}$$

#### **Relation between Bond Parameters:**

- Bond length 
$$\infty$$
 size of atom  $\infty$   $\frac{1}{\% s\text{-character}}$ 

$$\infty \frac{1}{\text{bond multiplicity}}$$

- Bond energy 
$$\propto \frac{1}{\text{bond length}}$$

$$\infty$$
% s-character  $\infty \frac{1}{\text{no. of lone pairs}}$ 

Bond angle ∞ % s-character

#### Valence Shell Electron Pair Repulsion (VSEPR) Theory

Bonded atoms in a molecule adopt that particular arrangement in space around the central atom which keeps them on the average as far as possible so that there are no further repulsions between them. As a result, molecule has minimum energy and maximum stability.

#### Postulates of VSEPR theory are:

- The shape of molecules can be determined by the number of electron pairs (bonding as well as non-bonding) in the valence shell of the central atom.
- Electron pairs in the valence shell repel one another and the order of repulsion is : lp - lp > lp - bp > bp - bp

- Electron pairs tend to occupy such positions in space that minimise repulsion and maximise distance between them.
- Where two or more resonance structures can represent a molecule, the VSEPR model is applicable to any such structure.

# PEEP INTO PREVIOUS YEARS

- Consider the following species: CN<sup>+</sup>, CN<sup>-</sup>, NO and CN. Which one of these will have the highest bond order?
  - (a) NO
- (b) CN (c) CN +

(NEET 2018)

- 10. Predict the correct order among the following:
  - (a) bond pair bond pair > lone pair bond pair

> lone pair - lone pair

- (b) lone pair bond pair > bond pair bond pair
  - > lone pair lone pair
- (c) lone pair lone pair > lone pair bond pair > bond pair - bond pair
- (d) lone pair lone pair > bond pair bond pair > lone pair - bond pair (NEET-I 2016)

#### VALENCE BOND THEORY (VBT)

- According to V.B.T., a covalent bond is formed between the two atoms by the overlap of half filled valence atomic orbitals of each atom containing one unpaired electron.
- The bond is formed when atoms approach each other in such a way that occupied orbitals with similar energies are able to overlap.
- Greater the overlap, stronger is the bond.

#### Types of Overlapping and Nature of Covalent Bonds:

- **Sigma** (σ) **Bond**: This type of covalent bond is formed by the end to end overlapping of bonding orbitals along the internuclear axis. The overlap is known as head on overlap or axial overlap.
- **Pi** ( $\pi$ ) **Bond**: This type of covalent bond is formed by the sidewise overlap of the half-filled atomic orbitals of bonding atoms. Such an overlap is known as sidewise or lateral overlap. The atomic orbitals overlap in such a way that their axis remain parallel to each other and perpendicular to the internuclear axis.
- During the formation of a  $\pi$ -bond, the overlapping occur to a smaller extent. Therefore, a  $\sigma$ -bond is stronger than a  $\pi$ -bond.

#### **H**YBRIDISATION

The process of mixing of atomic orbitals of nearly same energy to produce a set of entirely new orbitals of equivalent energy is known as hybridisation. The new orbitals thus formed are known as hybrid orbitals.

#### Some Important Conditions for Hybridisation:

- The orbitals present in the valence shell of the atom are hybridised.
- Orbitals undergoing hybridisation should have nearly same energies.
- Promotion of electron is not essential before hybridisation occurs.

#### Salient Features of Hybridisation:

- The number of hybrid orbitals are equal to the number of the atomic orbitals that get hybridised.
- The hybridised orbitals are always equivalent in energies and shapes.
- The hybrid orbitals are directed in space in some preferred direction to have minimum repulsion between the electron pairs.
- Hybridisation =  $\frac{1}{2}(V + M C + A)$

where, H = no. of orbitals involved in hybridisation viz. 2, 3, 4, 5, 6 and 7, hence nature of hybridisation will be sp,  $sp^2$ ,  $sp^3$ ,  $sp^3d$ ,  $sp^3d^2$ ,  $sp^3d^3$  respectively.

 $V = \text{no. of } e^- \text{ in valence shell of the central atom,}$ 

M = no. of monovalent atom,

C = charge on cation

A =charge on anion

#### MOLECULAR **O**RBITAL THEORY LINEAR COMBINATION OF ATOMIC ORBITALS (LCAO)

- Molecular orbital theory was developed by F. Hund and R.S. Mulliken in 1932. The salient features of this theory are:
- Molecular orbitals are formed by the addition or subtraction of wave functions of the atomic orbitals.
- Addition of wave functions during overlap of atomic orbitals leads to formation of bonding molecular orbitals with lower energy, they can be  $\sigma$  or  $\pi$ .
- Subtraction of wave functions during overlap of atomic orbitals leads to formation of anti-bonding molecular orbitals with higher energy, written as  $\sigma^*$  or  $\pi^*$ .
- Filling of electrons in molecular orbitals takes place in accordance with aufbau's principle, Hund's rule and Pauli's exclusion principle.

- Energy order for molecular orbitals upto N<sub>2</sub>:  $\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < (\pi 2p_x = \pi 2p_y) < \sigma 2p_z$  $< (\pi^* 2p_x = \pi^* 2p_y) < \sigma^* 2p_z$
- Energy order for molecules beyond N<sub>2</sub>:  $\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p_z < \pi 2p_x = \pi 2p_y$  $< \pi^* 2p_x = \pi^* 2p_y < \sigma^* 2p_z$
- Bond order: The number of covalent bonds formed in a molecule is called its bond order. Mathematically, it is defined as half of the difference between the number of bonding and anti-bonding electrons.

Bond order (B.O.) = 
$$\frac{1}{2} (N_b - N_a)$$

where,  $N_b$  is number of electrons present in bonding molecular orbitals and  $N_a$  is number of electrons present in anti bonding molecular orbitals.

- If  $N_b > N_a$ ; B.O. = +ve, the molecule is stable.
- If  $N_b < N_a$ ; B.O. = -ve, the molecule is unstable or does not exist.
- If  $N_b = N_a$ ; B.O. = 0, the molecule is unstable or does not exist.
- Isoelectronic species have same bond order.

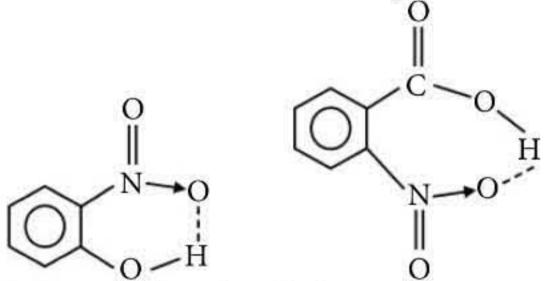
#### HYDROGEN BONDING

• When hydrogen atom is bonded to atoms of highly electronegative elements such as fluorine, oxygen or nitrogen, the Hydrogen atom forms a weak bond with the electronegative atom of the other molecule. This weak bond is called hydrogen bond. For example, hydrogen fluoride, HF,

$$--H$$
 $-F$  $--H$  $-F$  $---H$  $-F$  $---H$  $-F$  $----H$ 

#### **Types of Hydrogen Bonding**

- Intermolecular hydrogen bonding : Formed between different molecules of the same or different substances.
  - Example: HF, H<sub>2</sub>O, ROH (same compound) and hydrogen bonding between water and alcohol, or water and ammonia (different compounds), etc.
- Intramolecular hydrogen bonding: Hydrogen bond is formed between the hydrogen atom and the highly electronegative atom (F, O or N) present in the same molecule. Intramolecular hydrogen bond results in the cyclization of the molecule and prevents their association. Examples are:



Ortho-nitrophenol Ortho-nitro

Ortho-nitrobenzoic acid

#### PEEP INTO PREVIOUS YEARS

- 11. The type of hybridisation and number of lone pair(s) of electrons of Xe in XeOF<sub>4</sub>, respectively, are
  - (a)  $sp^3d$  and 2
- (b)  $sp^3d^2$  and 2
- (c)  $sp^3d^2$  and 1
- (d)  $sp^3d$  and 1

(JEE Main 2019)

- 12. Which one of the following compounds shows the presence of intramolecular hydrogen bond?
  - (a)  $H_2O_2$
  - (b) HCN
  - (c) Cellulose
  - (d) Concentrated acetic acid
- (NEET-II 2016)

#### **Answer Key For Peep Into Previous Years**

- l. (
- (b)

(d)

(c)

- 3.
- (A)

**(b)** 

10

WRAPitUP

(c)

- 5.
- **d**)
- (a,b)

(c)

# 1. In which of the following arrangements, the order is not according to the property indicated?

- (a)  $Al^{3+} < Mg^{2+} < Na^{+} < F^{-}$  (Increasing ionic size)
- (b) B < C < N < O (Increasing first ionisation energy)
- (c) I < Br < F < Cl (Increasing electron gain enthalpy)
- (d) Li < Na < K < Rb (Increasing metallic radius)
- 2. In which of the following species the underlined C-atom has  $sp^3$  hybridization?

- (b) CH<sub>3</sub>CH<sub>2</sub>OH (a)  $CH_2 = \underline{C}H - CH_3$
- (c) CH<sub>3</sub>COCH<sub>3</sub>
- (d) CH<sub>3</sub>COOH
- Among Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, P<sub>2</sub>O<sub>3</sub> and SO<sub>2</sub>, the correct order of acid strength is
  - (a)  $SiO_2 < SO_2 < Al_2O_3 < P_2O_3$
  - (b)  $Al_2O_3 < SiO_2 < SO_2 < P_2O_3$
  - (c)  $SO_2 < P_2O_3 < SiO_2 < Al_2O_3$
  - (d)  $Al_2O_3 < SiO_2 < P_2O_3 < SO_2$
- Which of the following is correct based on molecular orbital theory for peroxide ion?
  - (a) Its bond order is two and it is paramagnetic.
  - (b) Its bond order is two and it is diamagnetic.
  - (c) Its bond order is one and it is diamagnetic.
  - (d) Its bond order is one and it is paramagnetic.
- Consider the following statements:
  - I. The radius of an anion is larger than that of the parent atom.
  - II. The ionization energy generally increases with increasing atomic number in a period.
  - III. The electronegativity of an element is the tendency of an isolated atom to attract an electron.

Which of the above statements is/are correct?

- (a) I alone
- (b) II alone
- (c) I and II
- (d) II and III
- The bond order in NO is 2.5 while that in NO<sup>+</sup> is 3. Then
  - (a) bond length in NO > bond length in NO<sup>+</sup>
  - (b) bond length in  $NO^+$  = bond length in NO
  - (c) bond length in NO<sup>+</sup> > bond length in NO
  - (d) bond length is unpredictable.
- Following statements regarding the periodic trends of chemical reactivity of the alkali metals and the halogens are given. Which one of these is correct?
  - (a) The chemical reactivity decreases in alkali metals but increases in halogens with increase in atomic number, down the group.
  - (b) In alkali metals, the reactivity increases but in halogens, it decreases with increase in atomic number down the group.
  - (c) In both alkali metals and halogens, the chemical reactivity decreases with increases in atomic number down the group.
  - (d) The chemical reactivity increases with increase in atomic number down the group in both alkali metals and halogens.

- 8. The bond dissociation energy of B-F bond in BF<sub>3</sub> is 646 kJ mol<sup>-1</sup> whereas that of C-F in CF<sub>4</sub> is 515 kJ mol<sup>-1</sup>. The correct reason for higher B–F bond dissociation energy as compared to that of C-F is
  - (a) lower degree of  $p\pi$ - $p\pi$  interaction between B and F in BF<sub>3</sub> than that between C and F
  - (b) significant  $p\pi$ - $p\pi$  interaction between B and F in BF<sub>3</sub> whereas there is no possibility of such interaction between C and F in CF<sub>4</sub>
  - (c) stronger  $\sigma$  bond between B and F in BF<sub>3</sub> as compared to that between C and F in CF<sub>4</sub>
  - (d) smaller size of B atom as compared to that of C atom.
- The electronegativity difference between N and F is greater than that between N and H yet the dipole moment of NH<sub>3</sub> (1.5 D) is larger than that of NF<sub>3</sub> (0.2 D). This is because
  - (a) in NH<sub>3</sub> as well as NF<sub>3</sub> the atomic dipole and bond dipole are in opposite directions
  - (b) in NH<sub>3</sub> the atomic dipole and bond dipole are in the opposite directions whereas in NF<sub>3</sub>, these are in the same direction
  - (c) in NH<sub>3</sub> as well as in NF<sub>3</sub> the atomic dipole and bond dipole are in the same direction
  - (d) in NH<sub>3</sub>, the atomic dipole and bond dipole are in the same direction whereas in NF<sub>3</sub> these are in opposite direction.
- 10. Out of  $N_2O$ ,  $SO_2$ ,  $I_3^+$ ,  $I_3^-$ ,  $H_2O$ ,  $NO_2^-$  and  $N_3^-$ , the linear species are
  - (a)  $NO_2^-$ ,  $I_3^+$ ,  $H_2O$  (b)  $N_2O$ ,  $I_3^+$ ,  $N_3^-$

  - (c)  $N_2O$ ,  $I_3^-$ ,  $N_3^-$  (d)  $N_3^-$ ,  $I_3^+$ ,  $SO_2$
- 11. The electronic configuration of four elements are given below. Arrange these elements in the correct order of the magnitude (without sign) of their electron affinity.
  - (i)  $2s^2 2p^5$  (ii)  $3s^2 3p^5$  (iii)  $2s^2 2p^4$  (iv)  $3s^2 3p^4$
  - (a) (ii) < (i) < (iv) < (iii) (b) (i) < (iii) < (iv) < (ii)
  - (c) (i) < (ii) < (iv) < (iii) (d) (iii) < (iv) < (i) < (ii)
- 12. Molecular shapes of SF<sub>4</sub>, CF<sub>4</sub> and XeF<sub>4</sub> are
  - (a) same with 2, 0 and 1 lone pairs of electrons respectively
  - (b) same with 1, 1 and 1 lone pairs of electrons respectively
  - (c) different with 1, 0 and 2 lone pairs of electrons respectively
  - (d) different with 1, 1 and 1 lone pairs of electrons respectively.

**13.** For an element, *I.E.* values are

 $(I.E.)_1 = 738 \text{ kJ mol}^{-1} (I.E.)_2 = 1450 \text{ kJ mol}^{-1}$ 

 $(I.E.)_3 = 7.7 \times 10^3 \text{ kJ mol}^{-1} (I.E.)_4 = 1.1 \times 10^4 \text{ kJ mol}^{-1}$ this element belongs to

- (a) alkali metals
- (b) alkaline earth metals
- (c) chalcogens
- (d) halogens.
- 14. The correct order of the bond angles is
  - (a)  $NH_3 > H_2O > PH_3 > H_2S$ 
    - (b)  $NH_3 > PH_3 > H_2O > H_2S$
    - (c)  $NH_3 > H_2S > PH_3 > H_2O$
    - (d)  $PH_3 > H_2S > NH_3 > H_2O$
- 15. Which of the following order is wrong?
  - (a)  $NH_3 < PH_3 < AsH_3$
- Acidic
- (b) Li < Be < B < C  $(I.E._1)$

- (c)  $Al_2O_3 < MgO < Na_2O < K_2O Basic$
- (d)  $Li^+ < Na^+ < K^+ < Cs^+$  Ionic radius

(d) B

16. The table shown below gives the bond dissociation energies ( $E_{diss}$ ) for single covalent bonds of carbon (C) atoms with element A, B, C and D. Which element has the smallest atom?

Bond	$E_{\rm diss}$ (kJ mol <sup>-1</sup> )
C-A	240
C-B	328
C-C	276
C-D	485

- (a) C
- (b) D
- (c) A
- 17. A sudden large jump between the values of second and third ionisation energies of elements would be associated with which of the following electronic configurations?

  - (a)  $1s^2 2s^2 2p^6 3s^1$  (b)  $1s^2 2s^2 2p^6 3s^2 3p^1$  (c)  $1s^2 2s^2 2p^6 3s^2 3p^2$  (d)  $1s^2 2s^2 2p^6 3s^2$
- 18. The number of sigma ( $\sigma$ ) and pi ( $\pi$ ) bonds present in a molecule of tetracyanoethylene  $(CN)_2C = C(CN)_2$ are
  - (a)  $5\sigma$  and  $9\pi$
- (b)  $5 \sigma$  and  $8 \pi$
- (c)  $9\sigma$  and  $9\pi$
- (d)  $9 \sigma$  and  $7 \pi$ .
- 19. The electron affinity values (in kJ mol<sup>-1</sup>) of three halogens, x, y, and z are, respectively, -349, -333and -325. Then x, y and z are, respectively
  - (a)  $F_2$ ,  $Cl_2$  and  $Br_2$
- (b)  $Cl_2$ ,  $F_2$ , and  $Br_2$
- (c)  $Cl_2$ ,  $Br_2$  and  $F_2$
- (d)  $Br_2$ ,  $Cl_2$  and  $F_2$
- **20.** Which of the species  $CN^-$ ,  $O_2^-$ ,  $NO^+$  and  $CN^+$  have the same bond order?
  - (a)  $CN^-$  and  $O_2^-$
- (b) NO<sup>+</sup> and CN<sup>+</sup>
- (c)  $O_2^-$  and  $NO^+$
- (d) NO<sup>+</sup> and CN<sup>-</sup>

#### SOLUTIONS

1. (b): The order of  $I.E._1$  of B, C, O and N is as B < C < O < N

I.E.<sub>1</sub> of N (1s<sup>2</sup>, 2s<sup>2</sup>, 2p<sup>3</sup>) is more than that of O (1s<sup>2</sup>, 2s<sup>2</sup>, 2p<sup>4</sup>) due to the presence of extra stable half-filled 2*p*-subshell in the valence shell of N.

2. (b): C-atom forming 4 sigma bonds (zero  $\pi$  bond) is sp<sup>3</sup>-hybridised, C-atom forming 3 sigma and 1 pi bonds is  $sp^2$ -hybridised, and C-atom forming 2 sigma and 2 pi bonds is *sp*-hybridised.

3. (d): Acidic strength increases with the increase of non-metallic character which increases as we move across the period. Thus, the correct order is

$$Al_2O_3 < SiO_2 < P_2O_3 < SO_2$$

4. (c): The peroxide ion  $O_2^{2-}$  has 18 electrons arranged in the following manner:

$$KK\sigma 2s^2$$
,  $\sigma^* 2s^2$ ,  $\sigma 2p_z^2$ ,  $\pi 2p_x^2 = \pi 2p_y^2$ ,  $\pi^* 2p_x^2 = \pi^* 2p_y^2$ 

All the electrons are paired. Thus,  $O_2^{2-}$  ion is diamagnetic. Bond order = (bonding electrons - antibonding electron)/2 = (10 - 8)/2 = 1

- 5. (c)
- 6. (a): Bond order  $\propto \frac{1}{\text{Bond length}}$

Hence, bond length of  $NO > NO^+$ .

- 7. (b): In alkali metals, the reactivity increases on moving down the group due to decrease in the value of ionization enthalpy while in halogens, the reactivity decreases on moving down the group due to decrease in the value of reduction potential.
- **8. (b)**: In BF<sub>3</sub>, the octet of B is not complete. Thus, to get rid of electron deficiency, the empty  $2p_z$ orbital on B atom overlaps (sideon) with a full  $2p_z$  orbital on all the three F atoms (delocalized)  $p\pi$ - $p\pi$ back bonding.

10. (c):  $N_2O$  is linear as N = N = O $I_3$  is linear with 2 bp and 3 lp.

 $N_3^-$  is also linear and isoelectronic with  $CO_2$ .

11. (d): In general, electron affinity increases across the period on account of increase of  $Z_{\rm eff}$  while decreases on moving down the group on account of increase of size. Elements (i) and (iii) are succeeding members of the  $2^{\rm nd}$  period and belong to groups 17 and 16, respectively, while elements (ii) and (iv) are succeeding members of the  $3^{\rm rd}$  period and belong to groups 17 and 16, respectively. (i) is F, (ii) is Cl, (iii) is O, while (iv) is S. However, O and F have unexpectedly low electron affinities on account of relatively small size.

Thus, the correct order of electron affinity is O < S < F < Cl

12. (c):  $SF_4$  ( $sp^3d$ , trigonal bipyramidal with one equatorial position occupied by 1 lone pair)  $CF_4$  ( $sp^3$ , tetrahedral, no lone pair),  $XeF_4$  ( $sp^3d^2$ , square planar, two lone pairs).

**13. (b)**: 
$$(IE)_1 < (IE)_2 << (IE)_3 < (IE)_4$$

 $(IE)_3$  is very high thus,  $M^{2+}$  is stable with inert gas configuration. Thus, element belongs to alkaline earth metals.

**14. (a)**: The bond angles depend upon electronegativity of the central atom and number of lone pairs of electrons. Greater the electronegativity and more the number of lone pairs, smaller is the angle. Since, the electronegativities of N (3.0) and O (3.5) are close, but NH<sub>3</sub> has one and H<sub>2</sub>O has two lone pairs of electrons, therefore, bond angle in NH<sub>3</sub> is larger (107°) than in H<sub>2</sub>O (104.5°). Similarly, the electronegativities of P (2.1) and S (2.5) are close but PH<sub>3</sub> has one while H<sub>2</sub>S has two lone pairs of electrons, therefore, bond angle in PH<sub>3</sub> (93.4°) is little more than that in H<sub>2</sub>S (92.1°). Thus, the actual order is : NH<sub>3</sub> > H<sub>2</sub>O > PH<sub>3</sub> > H<sub>2</sub>S.

**15. (b)**:  $(I.E.)_1$  of Be > B

**16. (b)**: Smaller the atom, stronger is the bond and greater the bond dissociation energy. Therefore, the bond C-D has the greatest energy or D has smallest atom.

17. (d): A sudden large jump between the values of second and third ionisation energies indicates that the first two electrons are removed from the outermost shell while the third electron is removed from the stable configuration. This is possible only for  $1s^2 2s^2 2p^6 3s^2$ .

18. (c): 
$$N = C$$
 $\Sigma = C$ 
 $\Sigma =$ 

19. (b): The correct order of electron affinity values (in kJ mol<sup>-1</sup>)is

$$Cl(-349) > F(-333) > Br(-325)$$

**20.** (d): Total no. of electrons in  $CN^- = 6 + 7 + 1 = 14$ 

Total no. of electrons in  $O_2^- = 8 + 8 + 1 = 17$ 

Total no. of electrons in  $NO^+ = 7 + 8 - 1 = 14$ 

Total no. of electrons in  $CN^+ = 6 + 7 - 1 = 12$ 

As  $CN^-$  and  $NO^+$  contain the same total no. of electrons, their MO electronic configuration will be same.

Thus, CN<sup>-</sup> and NO<sup>+</sup> have the same bond order.



S E A R C H
C O T H E
I S G
E Z A
N U Z Z L E
C G R M I L
E W O R D S

Try to find as many as elements name. Readers can send their responses at editor@mtg.in or post us with complete address by  $10^{th}$  of every month. The name of the reader who will give more than twenty correct answer, will be published in next issue.

	U	M	U	D	1	Α	1	M	1	1	Α	Р	F	L	U	0	R	1	N	E	S	М	
	0	D	Υ	М	1	U	М	U	N	Ε	D	В	Υ	L	0	М	1	E	Е	E	U	C	
	Α	R	F	L	M	U	М	1	М	R	T	E	P	R	T	R	T	N	P	1	0	Ν	
Ì	1	М	L	R	R	Α	U	C	G	М	N	L	Ν	M	K	1	1	L	D	P	М	Ν	j
	М	М	В	R	0	М	1	N	Е	U	U	N	М	U	1	D	Α	N	Α	٧	0	D	
	U	М	U	G	U	Α	М	E	R	1	C	1	U	М	0	1	1	E	Ε	В	Ν	C	
1	Ĩ	U	U	1	Α	E	Υ	R	L	Ν	R	Α	D	1	U	М	G	U	R	T	0	Ν	
	М	1	N	1	N	D	D	W	М	U	1	S	S	Α	Τ	0	P	Α	T	Н	S	C	
	L	R	R	D	D	1	0	Α	М	T	T	D	S	1	L	1	C	0	N	Τ	M	U	
	0	U	E	0	U	0	Ε	L	D	P	Z	Ε	L	D	Ν	L	T	R	Н	U	1	R	
	Н	L	Н	G	N	Α	S	T	1	Ε	N	1	T	Α	T	S	Α	Α	U	M	U	1	
	Е	L	0	T	М	1	Α	1	S	N	М	U	N	1	T	Α	L	P	N	S	М	U	
	L	Е	R	P	Z	1	R	C	0	N	1	U	М	C	U	L	1	T	Н	1	U	M	
	Е	T	L	D	Υ	S	P	R	0	S	1	U	М	U	1	М	D	Α	C	В	U	L	
	Н	Р	S	0	Н	Р	0	Н	М	L	P	Е	М	U	1	N	Ε	L	Ε	S	М	М	
	D	М	0	М	0	В	T	Н	0	R	1	U	М	Ε	R	C	U	R	Y	Α	U	0	



Chapterwise practice questions for CBSE Exams as per the latest pattern and marking scheme issued by CBSE for the academic session 2019-20.

# Series 2

Classification of Elements & Periodicity in Properties/ Chemical Bonding and Molecular Structure Time Allowed : 3 hours Maximum Marks : 70

#### **GENERAL INSTRUCTIONS**

- (i) All questions are compulsory.
- (ii) Section A: Q. no. 1 to 20 are very short answer-objective questions and carry 1 mark each.
- (iii) Section B: Q. no. 21 to 27 are short answer questions and carry 2 marks each.
- (iv) Section C: Q. no. 28 to 34 are long answer-I questions and carry 3 marks each.
- (v) Section D: Q. no. 35 to 37 are long answer-II questions and carry 5 marks each.
- (vi) There is no overall choice in the question paper. However, internal choices are given in the sections.
- (vii) Use log tables if necessary, use of calculators is not allowed.

#### SECTION-A

- The decreasing order of the ionization potential of the following elements is
  - (a) Ne > Cl > P > S > Al > Mg
  - (b) Ne > Cl > P > S > Mg > Al
  - (c) Ne > Cl > S > P > Mg > Al
  - (d) Ne > Cl > S > P > Al > Mg
- 2. The hybridisation of atomic orbitals of nitrogen in  $NO_2^+$ ,  $NO_3^-$  and  $NH_4^+$  are
  - (a) sp,  $sp^2$  and  $sp^3$  respectively
  - (b) sp,  $sp^3$  and  $sp^2$  respectively
  - (c)  $sp^2$ , sp and  $sp^3$  respectively
  - (d)  $sp^2$ ,  $sp^3$  and sp respectively.
- 3. Among the following select the incorrect statement.
  - (a) The first ionization potential of Na is less than the first ionization potential of Mg.
  - (b) The second ionization potential of Mg is greater than the second ionization potential of Na.
  - (c) The first ionization potential of Al is less than the first ionization potential of Mg.

- (d) The third ionization potential of Mg is greater than the third ionization potential of Al.
- 4. What formal charges are present in the molecule  $C_6H_5C \equiv N O$ ?
  - (a) N is -1 and C is +1
  - (b) N is + 1 and C is 1
  - (c) O is 1 and C is + 1
  - (d) O is 1 and N is + 1
- 5. X has exceptional outer electronic configuration as  $4d^{10} 5s^0$ . It belongs to
  - (a) 4<sup>th</sup> period, group 11 (b) 5<sup>th</sup> period, group 10
  - (c) 6<sup>th</sup> period, group 9 (d) 3<sup>rd</sup> period, group 16
- 6. Which pair among the following is isostructural?
  - (a)  $XeF_2$ ,  $IF_2$
- (b) NH<sub>3</sub>, BF<sub>3</sub>
  - (c)  $CO_3^{2-}$ ,  $SO_3^{2-}$
- (d) PCl<sub>5</sub>, ICl<sub>5</sub>
- 7. Ionisation of energy F<sup>-</sup> is 320 kJ mol<sup>-1</sup>. The electron gain enthalpy of fluorine would be
  - (a)  $-320 \text{ kJ mol}^{-1}$ 
    - (b)  $-160 \text{ kJ mol}^{-1}$
  - (c)  $+ 320 \text{ kJ mol}^{-1}$
- (d)  $+ 160 \text{ kJ mol}^{-1}$

- 8.  $N_2$  and  $O_2$  are converted to monocations  $N_2^+$  and  $O_2^+$  respectively. Which is wrong?
  - (a) In  $N_2^+$ , the N N bond weakens.
  - (b) In  $O_2^+$ , the O O bond order increases.
  - (c) In  $O_2^+$ , paramagnetism decreases.
  - (d) N<sub>2</sub><sup>+</sup> becomes diamagnetic.
- The statement that is not true for the long form of the periodic table is
  - (a) it reflects the sequence of filling the electrons in the order of sub-energy levels *s*, *p*, *d* and *f*
  - (b) it helps to predict the stable valency states of the elements
  - (c) it reflects trends in physical and chemical properties of the elements
  - (d) it helps to predict the relative ionicity of the bond between any two elements.
- 10. In  $O_2^-$ ,  $O_2$  and  $O_2^{2-}$  molecular species, the total number of anti-bonding electrons respectively are
  - (a) 8, 6, 8
- (b) 6, 6, 6
- (c) 1, 0, 2
- (d) 7, 6, 8
- 11. Write the IUPAC name and symbol of an element having atomic number 118.

(NCT 2010, 2013, 2015)

- 12. Write two resonating structures of N<sub>2</sub>O that satisfy the octet rule.
- **13.** An element is present in the third period of *p*-block. It has 5 electrons in its outermost shell. Predict its group. How many unpaired electrons does it have?
- 14. BF<sub>3</sub> molecule has zero dipole moment although B—F bonds are polar. Why?
- 15. What is the most important cause of periodicity?
- 16. What is the total number of sigma and pi bonds in the following molecules?
  - (a)  $C_2H_2$
- **(b)**  $C_2H_4$
- 17. Define hybridisation.
- 18. How does ionisation enthalpy vary in the periodic table?
- 19. Predict the position of the element in the periodic table satisfying the electronic configuration  $(n-1)d^{1}ns^{2}$  for n=4.
- **20.** Write two factors responsible for formation of ionic bond.

#### **SECTION-B**

- 21. The electron gain enthalpy of bromine is 3.36 eV. How much energy in kcal is released when 8 g of bromine is completely converted to Br<sup>-</sup> ions in the gaseous state? (1 eV = 23.06 kcal mol<sup>-1</sup>).
- 22. Explain why  $CO_3^{2-}$  ion cannot be represented by a single Lewis structure. How can it be best represented?
- 23. A monoatomic anion with unit negative charge contains 45 neutrons and 36 electrons. What is the atomic mass of the element and in which group of the periodic table does it lie?

#### OR

Classify the following oxides as acidic, basic, amphoteric or neutral:

Na<sub>2</sub>O, CO<sub>2</sub>, CaO, Al<sub>2</sub>O<sub>3</sub>, N<sub>2</sub>O, NO<sub>2</sub>, ZnO and Cl<sub>2</sub>O<sub>7</sub>.

- 24. What shapes are associated with the following hybrid orbitals?
  - (a)  $sp^2$
- **(b)**  $sp^3d$
- (c) sp
- (d)  $sp^3d^2$
- 25. Why do halogens have the highest negative electron gain enthalpy in their respective periods?
- 26. Which out of NH<sub>3</sub> and NF<sub>3</sub> has higher dipole moment and why?

(NCERT, MSE Chandigarh 2008, KVS 2015, 2016)

#### OR

Draw molecular orbital diagram for He<sub>2</sub> and Li<sub>2</sub>.

- 27. (i) Out of Na<sup>+</sup> and Ne, which has higher ionisation enthalpy, and why?
  - (ii) A student reported the radii of Fe, Fe<sup>2+</sup> and Fe<sup>3+</sup> as 117 pm, 64 pm and 76 pm respectively. Do you agree with the reported values? Justify the answer.

#### **SECTION-C**

- 28. (a) Which of the following species has the shortest bond length?
  NO, NO<sup>+</sup>, NO<sup>-</sup>
  - (b) Find the bond order of  $C_2$ .
- **29.** The first  $(\Delta_i H_1)$  and the second  $(\Delta_i H_2)$  ionisation enthalpies (kJ mol<sup>-1</sup>) of three elements I, II and III are given below:

III403 549  $\Delta_i H_1$ 1142  $\Delta_i H_2$ 1060 2080 2640

Identify the element which is likely to be

- (a) a non-metal (b) an alkali metal
- (c) an alkaline earth metal.

#### OR

Select from each group the species which has the smallest radius stating appropriate reason.

- (a)  $O, O^-, O^{2-}$  (b)  $K^+, Sr^{2+}, Ar$  (c) Si, P, Cl
- 30. (a) Use molecular orbital theory to explain why Be<sub>2</sub> molecule does not exist.
  - (b) Compare the stability of  $O_2^+$  and  $O_2$  on the basis of molecular orbital theory.

(NCERT, KVS 2014, NCT 2015)

- **31.** Arrange the following
  - (i) Decreasing radii of ions : O<sup>2-</sup>, F<sup>-</sup>, Na<sup>+</sup>, Mg<sup>2+</sup>
  - (ii) Increasing first ionisation energy: Mg, Al, Si, Na
  - (iii) Increasing size : Cl<sup>-</sup>, S<sup>2-</sup>, Ca<sup>2+</sup>, Ar
- 32. Using VSEPR theory, identify the type of hybridisation and draw the structure of OF<sub>2</sub>. What are the oxidation states of O and F?

#### OR

Using VSEPR theory, draw and explain the shape of PCl<sub>5</sub> and BrF<sub>5</sub>.

- 33. (a) What is the basic difference between the terms electron gain enthalpy and electronegativity?
  - (b) What is modern periodic law?
- 34. Draw Lewis structures for the following molecules and ions.

F<sub>2</sub>, PH<sub>3</sub>, H<sub>2</sub>S, SiCl<sub>4</sub>, C<sub>3</sub>H<sub>8</sub>, Na<sup>+</sup>

#### SECTION-D

- 35. (a) Given reason:
  - (i)  $IE_2$  for alkali metals shows a jump whereas  $IE_3$ for alkaline earth metals shows a jump.
  - (ii) Be and Mg atoms do not impart colour in flame.
- **(b)** Calculate the bond length of C—X bond, if C—C bond length is 1.54 Å, *X*—*X* bond length is 1.00 Å and electronegativity values of C and X are 2.0 and 3.0 respectively.

OR

- (a) Give reason:
  - (i) Chlorine has maximum electron affinity.
  - (ii) The atomic radius decreases along the period but inert gases have maximum atomic radius in a period.

- (b) Ionization potential and electron affinity of fluorine are 17.42 and 3.45 eV respectively. Calculate the electronegativity of fluorine.
- **36.** Explain:
  - (a)  $XeF_2$  molecule is linear molecule but it is  $sp^3d$ hybridized.
  - (b) ClF<sub>3</sub> is a T-shape molecule while NF<sub>3</sub> has a trigonal pyramidal shape.
  - (c) Why is it that in the SF<sub>4</sub> molecule, the lone pair of electrons occupies an equatorial position in the overall trigonal bipyramidal arrangement in preference to the axial position?

#### OR

Mention the postulates of the VSEPR theory. On the basis of VSEPR theory, predict the shapes of

- (i) HgBr<sub>2</sub>
- (ii)  $H_2S$  (iii)  $[Ni(CN)_4]^{2-}$
- 37. (a) Predict the formulae of the stable binary compounds that would be formed by the combination of the following pairs of elements:
  - (i) Silicon and oxygen
  - (ii) Phosphorus and fluorine
  - (iii) Element 71 and fluorine.
- (b) State two significant features and two limitations of the Mendeleev's periodic table.

#### OR

- Give reason:
  - (i) Sulphur has lesser ionization enthalpy than phosphorus.
  - (ii) A cation is always smaller while the anion is always bigger than its parent atom.
  - (iii) Noble gases have large positive electron gain enthalpies.
- (b) Write short notes on
  - (i) merits of extended form of periodic table
  - (ii) screening effect.

#### **SOLUTIONS**

- 1. (b): Ionization energy increases from left to right in a period but *I.E.* of group 2 is more than group 13 and *I.E.* of group-15 is more than group-16. This is because of stable electronic configuration of group 2  $(ns^2)$  and group 15  $(ns^2np^3)$ . Thus, the order is Ne > Cl > P > S > Mg > Al
- (a)
- 3. (b):  $IE_2$  of Mg is lower than that of Na because in case of Mg<sup>+</sup>, 3s-electron has to be removed while in case of Na<sup>+</sup>, an electron from the stable inert gas configuration has to be removed.

4. (d): For nitrogen: Formal charge =  $5 - \frac{1}{2}(8) = +1$ 

For oxygen: Formal charge =  $6-6-\frac{1}{2}(2)=-1$ 

- 5. (b): The exceptional outer electronic configuration of X suggests that, in principle its configuration should have been  $4d^8 5s^2$ . As such it lies in  $5^{th}$  period and group 10.
- 6. (a): Both  $XeF_2$  and  $IF_2^-$  are linear with  $sp^3d$ -hybridisation.
- 7. (a) : *IE* and *EA* of an element are equal in magnitude but opposite in sign.
- $\therefore IE = -EA$
- 8. (d):  $N_2^+$  becomes paramagnetic.

 $N_2^+$ (13 electrons) : KK  $\sigma 2s^2 \sigma^* 2s^2 \pi 2p_x^2 = \pi 2p_y^2 \sigma 2p_z^1$ 

B.O. = 
$$\frac{7-2}{2}$$
 = 2.5, paramagnetic.

- 9. (b): It does not help to predict the stable valency states of the elements.
- 10. (d): Molecular orbital electronic configuration of these oxygen species are:

$$O_2^-$$
 (17 electrons) =  $\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2 \pi 2p_x^2 = \pi 2p_y^2$ ,  $\pi^* 2p_x^2 = \pi^* 2p_y^1$ 

Number of anti-bonding electrons = 7

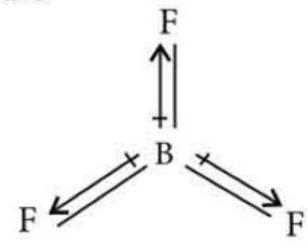
 $O_2$  (16 electrons) =

 $\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2 \pi 2p_x^2 = \pi 2p_y^2 \pi^* 2p_x^1 = \pi^* 2p_y^1$ Number of anti-bonding electrons = 6

$$O_2^{2-}$$
 (18 electrons) =  $\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2 \pi 2p_x^2 = \pi^* 2p_y^2 \pi^* 2p_x^2 = \pi^* 2p_y^2$ .

Number of anti-bonding electrons = 8

- 11. IUPAC name Oganesson, Symbol-Og
- 12.  $: \bar{N} = \bar{N} = \bar{O} : \longleftrightarrow : N \equiv \bar{N} \bar{O} :$
- 13. It belongs to the 15<sup>th</sup> group and is phosphorus. It has 3 unpaired electrons.
- **14.** In BF<sub>3</sub> molecule



BF<sub>3</sub> is symmetrical molecule, having zero resultant dipole moment.

15. Similarity in outer electronic configuration and gradual addition of an electron into the successive element, are the most important cause of periodicity.

16. (a)  $H \stackrel{\sigma}{=} C \stackrel{2\pi}{=} C \stackrel{\sigma}{=} H(3\sigma, 2\pi)$ 

(b) 
$$H \subset \frac{\sigma}{\pi} \subset \frac{\sigma}{\pi} \to H$$
 (5 $\sigma$ , 1 $\pi$ )

- 17. Mixing of atomic orbitals of slightly different energies of an atom to form a new set of atomic orbitals of equivalent energy and identical shape.
- 18. Ionisation enthalpy increases from left to right across a period but decreases from top to bottom in a group.

**19.** E.C. = 
$$(n-1)d^{1}ns^{2}$$
 if  $n=4$ 

Then,  $3d^14s^2$ 

Period – 4<sup>th</sup>, group – 3<sup>rd</sup>

20. Low ionisation energy and high electron affinity.

21. 
$$\frac{1}{2} Br_2 + e^- \longrightarrow Br^- + 3.36 \text{ eV}$$

Energy released from 80 g gaseous bromine  $= 3.36 \times 23.06$  kcal

- :. Energy released for conversion of 8 g gaseous bromine into Br ions  $\frac{3.36 \times 23.06 \times 8}{80} = 7.748$  kcal
- **22.**  $CO_3^{2-}$  is actually resonance hybrid of the following contributing structures:

$$\begin{bmatrix} O & O & O \\ C & \longleftrightarrow & C \\ O & O & O \end{bmatrix}^{2}$$

$$\begin{bmatrix} O & O \\ C & \longleftrightarrow & C \\ O & O \end{bmatrix}^{2}$$

$$I & III & IIII$$

If it were represented by a single structure, there would be two types of carbon-oxygen bonds, *i.e.*, C=O double bond and C-O single bond but actually, all the bonds are identical with same bond length and bond strength.

23. Number of neutrons = 45

Number of electrons in the anion = 36

 $\therefore$  Number of electrons in the atom = 36 - 1 = 35

Hence, atomic number = 35

Number of protons = 35

Atomic mass = Number of neutrons + Number of protons = 45 + 35 = 80

Electrons configuration (Z = 35):

 $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^5$ 

Hence, it belongs to group 17.

#### OR

Na<sub>2</sub>O, CaO : Basic

 $Al_2O_3$ , ZnO : Amphoteric  $N_2O$  : Neutral

CO<sub>2</sub>, NO<sub>2</sub>, Cl<sub>2</sub>O<sub>7</sub> : Acidic

24. (a)  $sp^2$  – Trigonal planar

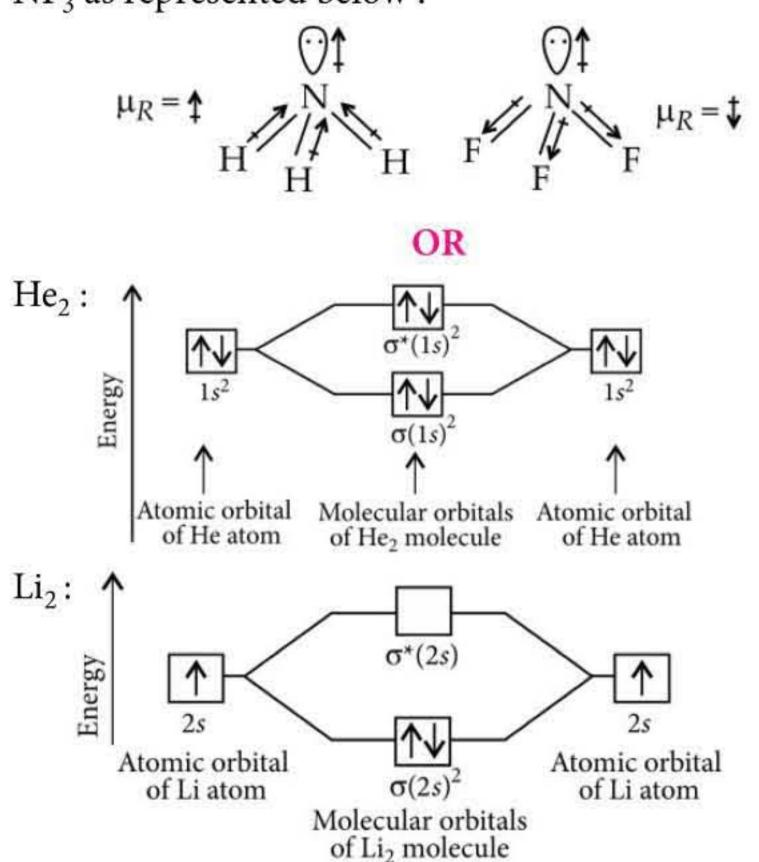
(b)  $sp^3d$  – Trigonal bipyramidal

(c) sp – Linear

(d)  $sp^3d^2$  – Octahedral

**25.** Halogens are towards the extreme right in a period. Therefore, they have small size and high effective nuclear charge. Hence, they have high tendency to gain electron. Also, the valence shell electronic configuration of halogens is  $ns^2np^5$  and as such they require one more electrons to acquire the stable noble gas configuration and so they have great tendency to accept an additional electron. So, they have the highest negative electron gain enthalpy in their respective period.

26. Although fluorine is more electronegative than nitrogen, the resultant dipole moment of NH<sub>3</sub> is greater than that of NF<sub>3</sub>. This is because, in case of NH<sub>3</sub> the orbital dipole due to lone pair is in the same direction as the resultant dipole moment of the N—H bonds whereas in NF<sub>3</sub> the orbital dipole is in the direction opposite to the resultant dipole moment of the three N—F bonds. The orbital dipole because of lone pair decreases the effect of the resultant N—F bond moment which results in low dipole moment of NF<sub>3</sub> as represented below:



**27.** (i) Na<sup>+</sup> and Ne are isoelectronic species but the nuclear charge on Na<sup>+</sup> (Z = 11) is more than on Ne (Z = 10). Therefore, electrons are held more tightly in Na<sup>+</sup> and so it has higher ionisation enthalpy.

(ii) No. As positive charge increases on metal ion ionic radius decreases and hence, reported radii are not true.

28. (a) The molecular orbital description of these species is as follows:

$$NO(7 + 8 = 15) = KK \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2 \pi 2p_x^2 = \pi 2p_y^2 \pi^* 2p_x^2$$

Bond order = 
$$\frac{1}{2}(8-3) = 2.5$$

$$NO^{+}(14) = KK \sigma 2s^{2} \sigma^{*} 2s^{2} \sigma 2p_{z}^{2} \pi 2p_{x}^{2} = \pi 2p_{y}^{2}$$

Bond order = 
$$\frac{1}{2}(8-2) = 3$$

$$NO^{2+}(13) = KK \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2 \pi 2p_x^2 = \pi 2p_y^1$$

Bond order = 
$$\frac{1}{2}(7-2) = 2.5$$

$$NO^{-}(16) = KK \sigma 2s^{2}\sigma^{*}2s^{2}\sigma 2p_{z}^{2}\pi 2p_{x}^{2} = \pi 2p_{y}^{2}\pi^{*}2p_{x}^{2}$$

Bond order = 
$$\frac{1}{2}(8-4) = 2$$

Thus, NO<sup>+</sup> has the highest bond order and therefore, has the shortest bond length.

**(b)** 
$$C_2(12) \rightarrow KK \sigma 2s^2 \sigma^* 2s^2 \pi 2p_x^2 = \pi 2p_y^2$$

Bond order = 
$$\frac{1}{2}(6-2)=2$$

29. (a) Element III is a non-metal. Ionisation enthalpies of non-metals are very high.

(b) An alkali metal has very low first ionisation enthalpy, and much higher second ionisation enthalpy. Therefore element I is an alkali metal.

(c) The  $\Delta_i H_1$  of element II is higher than that of element I and lower than that of element III, therefore it is an alkaline earth metal.

#### OR

(a) O has the smallest radius in this series. Addition of electron(s) to O atom causes a decrease in the effective nuclear charge. As a result, the electron cloud expands and the anion becomes bigger than the atom.

**(b)** Ar has the smallest radius in this series. In Ar there are only three shells of electrons, whereas K<sup>+</sup> has three shells but increased nuclear charge. Sr<sup>2+</sup> has four shells of electrons.

(c) Cl atom is the smallest in this series. This is because of the increase nuclear charge in going from Si, P to Cl.

30. (a) Beryllium atom has electronic configuration  $1s^2 2s^2$ . So, in Be<sub>2</sub> there are total eight electrons which must be filled in four molecular orbitals. M.O. electronic configuration of Be<sub>2</sub>:  $\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2$ 

B.O. = 1/2(4 - 4) = 0. Since the bond order is zero it shows that molecular beryllium will not exist.

(b) Stability of  $O_2^+$  and  $O_2^+$ :

Species	Total electrons	Configuration	Bond order
O <sub>2</sub>	16	KK $\sigma(2s)^2 \sigma^*(2s)^2$ $\sigma(2p_z)^2 \pi(2p_x)^2 = \pi(2p_y)^2$ $\pi^*(2p_x)^1 = \pi^*(2p_y)^1$	$\frac{(8-4)}{2} = 2.0$
O <sub>2</sub> <sup>+</sup>	15	KK $\sigma(2s)^2 \sigma^*(2s)^2$ $\sigma(2p_z)^2 \pi(2p_x)^2 = \pi(2p_y)^2$ $\pi^*(2p_x)^1$	$\frac{(8-3)}{2} = 2.5$

Greater the bond order, greater is stability.

31. (i) Ion
$$O^{2-}$$
> $F^-$ > $Na^+$ > $Mg^{2+}$ Radii (pm)1401369565(ii) ElementNaIE\_1 (kJ mol $^{-1}$ )496577738785(iii) Ion $Ca^{2+}$ Cl^- $\approx$  $S^{2-}$ Size (pm)99154184184

#### 32. The Lewis structure of $OF_2$ is :F:O:F:

There are four pairs of electrons (two lone pairs and two bond pairs) around the central O atom. According to VSEPR theory, these electron pairs must be arranged tetrahedrally. Since F F the hybrid orbitals arranged tetrahedrally are obtained by  $sp^3$  hybridization, the oxygen atom involves  $sp^3$  hybrid orbitals in bonding with fluorine. The molecule of  $OF_2$  is V-shaped with F-O-F bond angle of  $103^\circ18'$ . The normal tetrahedral angle of  $109^\circ28'$  is decreased because of the strong repulsion of bond pairs by the two lone pairs of electrons.

Oxidation number of F = -1 and O = +2

OR

Compound	No. of electrons pairs around the central atom	No. of atoms bounded to the central atom	Geometry/ shape		
PCl <sub>5</sub>	5 (5 electrons from P and 5 electrons from five Cl atoms)	5 Trigonal bipyramidal	Cl Cl Cl Cl Cl Cl Cl		
BrF <sub>5</sub>	6 (7 electrons from Br and 5 electrons from five F atoms)	5 Square pyramidal	F F F		

**33.** (a) The basic difference between the terms electron gain enthalpy and electronegativity is described below :

The electron gain enthalpy is the change in enthalpy for the reaction

$$X_{(g)} + e^{-} \longrightarrow X_{(g)}$$

Thus, electron gain enthalpy provides a measure of ease with which an atom adds an electron to form an anion. It is a measurable property.

Electronegativity is not a measurable quantity. It indicates a quantitative measure of the tendency of an atom in a compound to attract the shared electrons towards itself.

(b) Modern periodic law: "The physical and chemical properties of the elements are the periodic function of their atomic numbers, *i.e.*, when elements are arranged in increasing order of atomic numbers, the elements having similar properties are repeated after certain regular intervals".

34. (i):
$$\ddot{F} \cdot + \dot{F} : \longrightarrow \ddot{F} \cdot \ddot{F} :$$

(Lewis structure of  $F_2$ )

(ii)  $\dot{P} \cdot + 3H \times \longrightarrow H^{\times} \dot{P}^{\times} H$ 
 $\dot{H}$ 

(Lewis structure of  $PH_3$ )

(iii)  $\dot{S} \cdot + 2 \times H \longrightarrow H^{\times} \dot{S} \times H$ 

(Lewis structure of  $H_2S$ )

 $\dot{C}l:$ 

(iv)  $\times \dot{S} \times + 4 : \dot{C}l: \longrightarrow \dot{C}l^{\times} \dot{S} \times \dot{C}l:$ 
 $\dot{C}l:$ 

(Lewis structure of  $\dot{S} \times \dot{C} \times \dot{C} \times \dot{C} = \dot{C} \times \dot{C} \times \dot{C} = \dot{C} \times \dot{C} \times \dot{C} \times \dot{C} = \dot{C} \times \dot{C} \times$ 

(Lewis structure of C<sub>3</sub>H<sub>8</sub>)

- (vi) The Lewis structure of Na<sup>+</sup> is, Na<sup>+</sup>.
- **35.** (a) (i) The jump in IE values are noticed when the successive removal of electrons occurs from different shells. In alkali metals (n') removal of I and II electrons occurs from n, (n-1) shells respectively and thus shows a jump in  $IE_2$  values. This condition occurs during removal of II and III electrons from alkaline earth metals.
- (ii) Be and Mg atoms are comparatively smaller and their ionization energies are very high. Hence, their electrons are not excited by the energy of the flame to higher energy state. Therefore, these elements do not give any colour in flame.
- (b) C—C bond length = 1.54 ÅX - X bond length = <math>1.00 Å

$$r_{\rm C} = \frac{1.54}{2} = 0.77 \,\text{Å}$$
;  $r_{\rm X} = \frac{1.00}{2} = 0.50 \,\text{Å}$ 

C—X bond length,

$$d_{C-X} = r_C + r_X - 0.09 (X_X - X_C)$$
  
= 0.77 + 0.50 - 0.09(3 - 2)  
= 1.18 Å

#### OR

- (a) (i) Cl has more negative electron gain enthalpy than F. The less negative electron gain enthalpy of F is due to its very small size which has strong electron-electron repulsions. Therefore, F has less tendency to accept an electron and its electron gain enthalpy is less negative than Cl.
- (ii) Atomic radii of inert gases are van der Waals' radii whereas for rest all atoms covalent radii are determined experimentally. van der Waals' radii is greater in comparison to covalent radii.
- (b) According to Mulliken equation

$$X = \frac{IE + EA}{5.6}$$
 (when both *IE* and *EA* are taken in eV)  
 $X_{\rm F} = \frac{17.42 + 3.45}{5.6} = 3.726$ 

- **36.** (a) Due to  $sp^3d$  hybridisation, it has trigonal bipyramidal geometry in which three positions are occupied by lone pairs of electrons. The lone pairs are present in equatorial positions and their resultant effect is zero. As a result, the bonds are formed by axial Xe F bonds only which are at an angle of  $180^\circ$  to each other.
- **(b)** In  $ClF_3$ , , the central atom Cl has five electron pairs (three are bond pairs and two are lone pairs). It is a  $AX_3L_2$  type molecule where two lone pairs and one bond pair are arranged in equatorial position while two bond pair are arranged in axial position giving T-shape  $ClF_3$  molecule .  $NF_3$  is  $AX_3L$  type molecule and has a trigonal pyramidal shape.
- (c) In SF<sub>4</sub>, the central S atom has five electron pairs (four bond pairs and one lone pair) whose arrangement should be trigonal bipyramidal. However, one of the electron pairs is lone pair. SF<sub>4</sub> can, therefore, have structure (a) or structure (b).

$$F - \begin{picture}(100) \put(0.5){\line(100) \put(0.$$

In structure (i), there are three lp-bp repulsions at 90°. In structure (ii), there are only two lp-bp repulsions at 90°. Hence, structure (ii) is favoured one. The structure (ii) is known as see-saw shape.

#### OR

The main postulates of VSEPR theory are as follows:

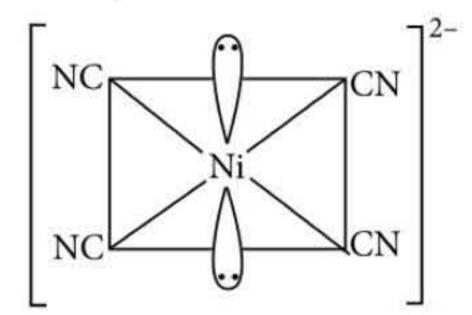
- (a) The shape of a molecule depends upon the number of valence shell electron pairs (bonded and non-bonded) around the central atom.
- (b) Pairs of electrons in the valence shell repel one another since their electron clouds are negatively charged.
- (c) These pairs of electrons tend to occupy such positions in space that minimise repulsion and thus maximise distance between them.
- (d) The valence shell is taken as a sphere with the electron pairs localising on the spherical surface at maximum distance from one another.
- (e) A multiple bond is treated as if it is a single electron pair and the two or three electron pairs of a multiple bond are treated as a single super pair.
- (f) Where two or more resonance structures can represent a molecule, the VSEPR model is applicable to any such structure.
- (i) Hg has only two electrons in its outermost orbit and sharing these electrons with two Br gives 2 pairs of electrons around Hg. This gives a linear structure of HgBr<sub>2</sub>.

$$: \dot{B}r \cdot \times Hg \times \dot{B}r : \longrightarrow Br - Hg - Br$$

(ii) S has 6 electrons in its outermost shell. 2H-atoms contribute 2 electrons during bonding. Thus, there are 8 electrons or 4 electron pairs around S. This gives a tetrahedral distribution of electron pairs around S. The two corners of the tetrahedron are occupied by H-atoms and the other two by lone pairs of electrons. Thus,  $H_2S$  is a bent structure molecule.

N	onthly	Test	Drive	CLA	SS XII	A	NSW	/ER	KEY
1.	(b)	2.	(c)	3.	(b)	4.	(c)	5.	(d)
6.	(b)	7.	(b)	8.	(c)	9.	(a)	10.	(c)
11.	(a)	12.	(a)	13.	(b)	14.	(c)	15.	(b)
16.	(a)	17.	(b)	18.	(d)	19.	(b)	20.	(b,c)
21.	(b,d)	22.	(b,c,d)	23.	(b,c)	24.	(5)	25.	(24.21)
26.	(3)	27.	(d)	28.	(b)	29.	(a)	30.	(b)

(iii) The four bond pairs in  $[Ni(CN)_4]^{2-}$  are distributed in a square planar distribution. The two lone pairs are in a direction at right angles to this plane. Thus, giving a square planar shape to such molecules.



- 37. (a) (i) Silicon oxide (SiO<sub>2</sub>)
- (ii) Phosphorus pentafluoride (PF<sub>5</sub>)
- (iii) Element with atomic number 71 is lutetium and forms lutetium fluoride (LuF<sub>3</sub>).
- (b) The two significant features of the Mendeleev's periodic table are as follows:
- (i) Mendeleev's periodic table made the study of elements and their compounds easier by systematically arranging elements in the increasing order of their atomic masses.
- (ii) Mendeleev left some gaps in his periodic table which provided a guide for discovery of new elements. For example, there were gaps below aluminium (eka-aluminium) and silicon (eka-silicon) which were later on discovered to be gallium and germanium, respectively.

Limitations of Mendeleev's periodic table:

- (i) Position of hydrogen: In Mendeleev's periodic table, hydrogen is placed in group IA, although it shows similarly in properties with the elements of group IA as well as with the elements of group VII A. Therefore in this periodic table, the position of hydrogen is not clearly defined.
- (ii) Inversion in the periodic table: In order to satisfy the periodic law, in this table certain pairs of elements had to be placed in the reverse order of atomic weights *e.g.*, cobalt (atomic weights 58.9) has been placed before nickel (with atomic weight 58.7).

#### OR

(a) (i) Due to more stable electronic configuration of P, it has greater ionisation enthalpy.

Electronic configuration of S = [Ne]  $3s^23p^4$ 

Electronic configuration of P = [Ne]  $3s^23p^3$ 

(ii) A cation is smaller than its parent atom because it has fewer electrons while its nuclear charge remains the same. The size of an anion will be larger than that of the parent atom because the addition of one or more electrons would result in increased repulsion among the electrons and a decrease in effective nuclear charge. (iii) It is due to stable electronic configuration of noble gases and because of interelectronic repulsion, addition of electrons is an endothermic process, as energy is needed to overcome repulsion.

#### (b) (i) Advantages of long form of periodic table:

- 1. This table removed the anomalies of inversions that existed in the Mendeleev's periodic table.
- 2. In this table same position is allotted to each isotope of an element as all the isotopes of an element have same atomic number.
- 3. Other anomalies of Mendeleev's periodic table like grouping of dissimilar elements together and similar elements separately has also been removed by this table.
- 4. It also explains the cause of periodicity on the basis of electronic configuration.
- (ii) Screening effect: Decrease in force of attraction exerted by nucleus on valence electron due to presence of electrons in inner shells is known as screening or shielding effect. The outermost electrons are shielded or screened from the nucleus by the inner electrons. Actual charge felt by outermost electrons is called the effective nuclear charge.

Effective nuclear charge  $(Z_{eff}) = Z - S$ where, Z = nuclear charge, S = screening constant Value of screening constant can be determined by Slater's rule.



# MONTHLY TEST

his specially designed column enables students to self analyse their extent of understanding of specified chapters. Give yourself four marks for correct answer and deduct one mark for wrong answer. Self check table given at the end will help you to check your readiness.

# Organic Chemistry: Some Basic Principles and Techniques

Total Marks: 120 Time Taken: 60 Min.

#### Only One Option Correct Type

- Homolytic fission of carbon-carbon bond of ethane produces an intermediate in which the carbon atom is in
  - (a)  $sp^2$ -hybridized state (b)  $sp^3$ -hybridized state
  - (c) sp-hybridized state (d) dsp<sup>2</sup>-hybridized state.
- Organic compound,  $A \xrightarrow{\text{HNO}_3/\text{AgNO}_3}$  white ppt. A can be

(a) 
$$\left(\begin{array}{c} \\ \end{array}\right)$$

- all of these.
- 3. Which of the following molecule/ion cannot be stabilized by hyperconjugation?

  - (a)  $CH_3CH = CH_2$  (b)  $(CH_3)_3C CH_2$
  - (c)  $(CH_3)_3C$
- (d) CH<sub>3</sub>CH<sub>2</sub>
- 2,2,3,3-Tetramethylbutane reacts with Cl<sub>2</sub> in such a way that one H-atom is replaced by Cl atom. IUPAC name of the product obtained is
  - (a) 2-chloromethyl-2,2,3-trimethylbutane
  - (b) 1-chloro-2,2,3,3-tetramethylbutane
  - (c) both are acceptable
  - (d) none is acceptable.
- The IUPAC name of the compound with formula  $C_nH_{2n+2}$ , having the lowest possible molecular mass and capable of showing enantiomerism is

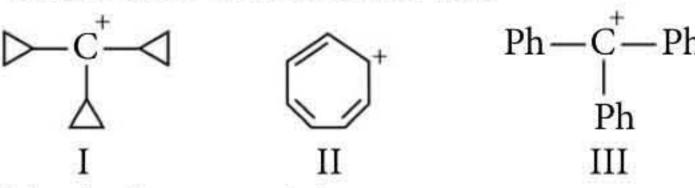
  - (a) 3-methyl hexane (b) 2,3-dimethyl pentane
  - (c) 2-methyl pentane (d) both (a) and (b).

- A compound which does not give a positive Lassaigne's test for nitrogen is
  - (a) glycine
- (b) hydrazine
- (c) urea
- (d) phenyl hydrazine.
- In the following carbocation, H/CH<sub>3</sub>, that is most likely to migrate to the positively charged C is

- (a)  $CH_3$  at C-4
- (b) H at C 4
- (c)  $CH_3$  at C 2
- (d) H at C-2
- Which of the following is the most stable resonance structure?

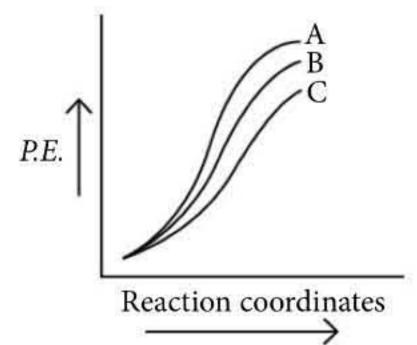
(a) 
$$H_2C$$
 $\ddot{O}H$ 
 $\ddot$ 

In the following graph, stability of different carbocations have been shown:



Match the potential energy curve with carbocation.

- II III
- (a) A
- (b) B A C
- (d) C



- 10. Which of the following is not an isomerisation reaction?
  - (a)  $3CH \equiv CH \xrightarrow{\text{Red hot}} C_6H_6$
  - (b)  $CH_3CH_2C \equiv CH \xrightarrow{NaNH_2} CH_3C \equiv CCH_3$
  - (c) cis-But-2-ene  $\rightleftharpoons trans$ -But-2-ene
  - (d)  $CH_3CH_2CH_2Br \xrightarrow{Anhyd.} CH_3CHCH_3$   $RACH_3CH_3CH_3CH_3$   $RACH_3CH_3CH_3CH_3$   $RACH_3CH_3CH_3CH_3$
- 11. Consider the following reactions:

Ph Cl 
$$\xrightarrow{95\% \text{ acetone}}$$
 Ph OF Me

(H) Me  $\xrightarrow{5\% \text{ H}_2\text{O}}$  Me

(II)  $\xrightarrow{90\% \text{ acetone}}$  Me

$$10\% \text{ H}_2\text{O}$$

$$(III)$$

$$80\% \text{ acetone} + 20\% \text{ H}_2\text{O}$$

$$(IV) 100\% \text{ H}_2\text{O}$$

Arrange the above reactions in the decreasing order of greater proportion of inverted product and select the correct option.

- (a) (I) > (II) > (III) > (IV)
- (b) (II) > (I) > (III) > (IV)
- (c) (III) > (II) > (IV)
- (d) (IV) > (III) > (II) > (I)
- 12. 0.5 g of an organic substance containing phosphorous was heated with conc. HNO<sub>3</sub> in the Carius tube. The phosphoric acid thus formed was precipitated with magnesia mixture as MgNH<sub>4</sub>PO<sub>4</sub> which on ignition gave a residue of 1.0 g of magnesium pyrophosphate (Mg<sub>2</sub>P<sub>2</sub>O<sub>7</sub>). The percentage of phosphorous in the organic compound is
  - (a) 55.85 %
- (b) 29.72 %
- (c) 19.18 %
- (d) 20.5 %

#### Assertion & Reason Type

**Directions**: In the following questions, a statement of assertion is followed by a statement of reason. Mark the correct choice as:

- (a) If both assertion and reason are true and reason is the correct explanation of assertion.
- (b) If both assertion and reason are true but reason is not the correct explanation of assertion.
- (c) If assertion is true but reason is false.
- (d) If both assertion and reason are false.
- 13. Assertion: In organic layer test, Cl<sub>2</sub> water is added to the sodium extract, which oxidises Br<sup>-</sup> and I<sup>-</sup> ions to Br<sub>2</sub> and I<sub>2</sub>, respectively.

**Reason :** Reduction potential of  $Cl_2$  is greater than that of  $Br_2$  and  $I_2$ .

14. Assertion: Relative reactivity towards electrophilic addition of

$$OCH_3$$
  $OCH_3$   $OCH_$ 

**Reason**: More the +M effect, less is stability of carbocation.

**15. Assertion**: Enol form of cyclohexane −1, 3, 5 trione is more stable than its keto form.

**Reason**: Enol form contains  $\alpha$ -hydrogen atoms.

#### JEE MAIN / ADVANCED

#### Only One Option Correct Type

16. For the reaction,

I. 
$$\langle -Cl \rightarrow \rangle + Cl^{-}, \Delta H_{1}^{\circ}$$

II.  $\langle -Cl \rightarrow \rangle + Cl^{-}, \Delta H_{2}^{\circ}$ 

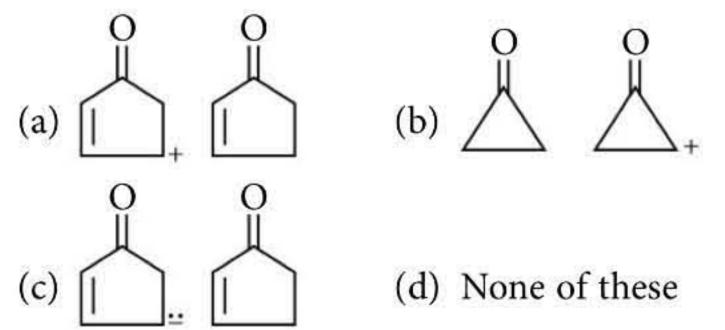
III.  $\langle -Cl \rightarrow \rangle + Cl^{-}, \Delta H_{2}^{\circ}$ 

IV.  $\langle -Cl \rightarrow \rangle + Cl^{-}, \Delta H_{4}^{\circ}$ 

The correct decreasing order of enthalpies of reaction for producing carbocation is

- (a)  $\Delta H_1^{\circ} > \Delta H_2^{\circ} > \Delta H_3^{\circ} > \Delta H_4^{\circ}$
- (b)  $\Delta H_4^{\circ} > \Delta H_1^{\circ} > \Delta H_2^{\circ} > \Delta H_3^{\circ}$
- (c)  $\Delta H_3^{\circ} > \Delta H_2^{\circ} > \Delta H_1^{\circ} > \Delta H_4^{\circ}$
- (d)  $\Delta H_2^{\circ} > \Delta H_1^{\circ} > \Delta H_4^{\circ} > \Delta H_3^{\circ}$
- 17. Identify the compound, which does not have a stereocenter?

18. Among the given pairs, in which pair second compound has less enol content than first compound?



- 19. Which of the following species behave both as a nucleophile and as an electrophile?
  - (i) CH<sub>3</sub>C≡N:
- (ii) CH<sub>4</sub>
- (iii)  $H_2C = \ddot{O}$ :
- (iv) R O R
- (a) (i) and (iii)
- (b) (i) and (ii)
- (c) (iii) and (iv)
- (d) (ii) and (iv)

#### More than One Options Correct Type

**20.** Which of the following statements are incorrect?

(a) : N is more basic than 
$$(CH_3)_3N$$
:

(b) Cl forms white precipitate with

 $Ag_{(aq)}^+$  most readily.

structures to each other.

- 21. Which of the following statements are correct?
  - (a) When a Lassaigne's solution is heated with dil. HNO<sub>3</sub>, cooled, and AgNO<sub>3</sub> solution is added, a pale yellow precipitate, partially soluble in NH<sub>3</sub> or NH<sub>4</sub>OH, indicates the presence of iodine in organic compound.
  - (b) When (CH<sub>3</sub>COO)<sub>2</sub>Pb solution is added to the acidified Lassaigne's extract of an organic compound containing sulphur, a black precipitate of PbS is formed.
  - (c) An organic compound containing N, on heating with conc. H<sub>2</sub>SO<sub>4</sub> gives (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> which liberates NH<sub>3</sub> on treatment with excess of NaOH.
  - (d) The molecular mass of a non-volatile organic compound is determined either by Dumas method or by Victor Meyer's method.
- **22.** In which of the following,  $\Delta G$  decreases if there can be some intramolecular rearrangement?

(a) 
$$\left(\begin{array}{c} \\ \\ \end{array}\right)$$
  $\stackrel{\scriptscriptstyle +}{\mathrm{CH}}_2$ 

(c) 
$$\stackrel{\text{Me}}{\searrow}$$
  $\stackrel{\text{+}}{\sim}$   $\stackrel{\text{+}}{\sim}$ 

(d) 
$$\langle \bigcirc \rangle$$
  $-\dot{C}H_2$ 

23. Which are correct statements?

(a) 
$$\bigcirc$$
 O and O  $\bigcirc$  are enantiomers.

are same structures.

- Argol (sod. potassium tartarate) will show optical isomerism.
- CH<sub>3</sub>CHO on reaction with HCN gives racemic mixture.

#### Numerical Value Type

24. Amongst the following, the total number of compounds for which Kjeldahl's method is not applicable.

PhNO<sub>2</sub>, Ph
$$-N = N-Ph$$
, PhNHCOPh,  $\bigcirc$ , PhNH<sub>2</sub>, Acetone,  $\bigcirc$  H Ethane nitrile, Urea

25. Amongst the following, the total number of reactions which follow S<sub>N</sub>1 mechanism are

(a) Me OTs + Cl<sup>-</sup> 
$$\xrightarrow{\text{CH}_3\text{OH}}$$
Me
(b) Me Br + CH<sub>3</sub>COO<sup>-</sup>  $\xrightarrow{\text{CH}_3\text{COOH}}$ 

(c) Me 
$$H_2O \xrightarrow{H_2O} EtOH$$
 OMe

(d) 
$$\longrightarrow$$
 +  $\bar{S}H \xrightarrow{DMF}$ 

(e) 
$$CH_3I + Me \rightarrow O^- \xrightarrow{t-BuOH} Me$$

(f) 
$$\sim$$
 Cl + CH<sub>3</sub>OH  $\xrightarrow{\text{CH}_3\text{OH}}$ 

(g) 
$$\sim$$
 Cl + CH<sub>3</sub>COO<sup>-</sup>  $\sim$  CH<sub>3</sub>COOH

(h) 
$$Me + CH_3CH_2OH \xrightarrow{EtOH}$$

26. Amongst the following, how many of them will show keto-enol tautomerism?

CH<sub>3</sub>COCH<sub>3</sub>, CH<sub>3</sub>CHO, CH<sub>3</sub>CH<sub>2</sub>CHO, CH<sub>3</sub>COCH<sub>3</sub>, CH<sub>3</sub>CH<sub>2</sub>CHO, CH
$$_3$$
COCH $_3$ 

#### Matrix Match Type

Answer the following questions (27 and 28) by appropriately matching the columns based on the information given in the passage:

In electron deficient reaction, intermediates carrying a positive charge on the carbon atom which has only six electrons in its valence shell, are called carbocations, whereas in electron rich reaction, intermediates carrying a negative charge on the carbon atom which possesses eight electrons in its valence shell, are called carbanions. Free radicals are neutral reaction intermediates (atoms or group of atoms) possessing an unpaired (odd) electron, whereas neutral divalent species having an unshared pair of electrons on carbon atom are called carbene. e.g., :  $CH_2$  :  $CCl_2$ , etc.

	Column-I		Column-II
P.	$\begin{array}{c} Ph_{II_{1}} \\ Ph_{II_{2}} \\ Ph_{II_{3}} \\ Ph_{II_{3$	I	Carbanion
Q.	$OH$ $CH_3$ $CH_3$ $CH_3$ $CH_3$	II	Free radical
R.	$H + R_3 N \xrightarrow{\Delta}$	III	Carbene
S.	$\langle \bigcirc \rangle$ Hg—CBr <sub>3</sub> $\xrightarrow{\Delta}$	IV	Carbocation

- 27. Which of the following has the correct combination considering column I and column II? (a) P, IV (b) Q, I (c) R, II
- 28. Which of the following has the correct combination considering column I and column II?

(b) Q, II (c) S, IV (a) R, I

(d) P, III

(d) S, III

Answer the following questions (29 and 30) by appropriately matching the columns based on the information given in the passage:

Reactions in which an unsaturated system (C = C,  $C \equiv C$ , C = O, etc) is saturated or partially saturated by addition of a molecule across the multiple bond are called addition reactions, whereas reactions in which there is replacement of one atom or group in a molecule by another atom or group are called substitution reactions.

	Column-I		Column-II
P.	$\begin{array}{c} \begin{array}{c} \begin{array}{c} \\ \\ \end{array} \end{array} \begin{array}{c} \\ \\ \end{array} \begin{array}{c} \\ \end{array} \begin{array}{c} \\ \\ \end{array} \begin{array}{c} \\ \end{array} \begin{array}$	1.	Racemic
Q.	OH OH	2.	Addition reaction
R.	$\begin{array}{c c} O & \text{(i) } \text{LiAlH}_4\\ \hline \\ CH_3 & \text{(ii) } \text{H}_3\text{O}^+\\ \hline \\ OH & \\ \hline \\ CH_3 & \\ \end{array}$	3.	Substitution reaction
S.	$HS \longrightarrow Cl \xrightarrow{Base} \left\langle S \right\rangle$	4.	Carbocation intermediate

29. Which of the following has the correct combination considering column I and column II?

(a) Q, 3 (b) P, 4 (c) R, 1, 2 (d) S, 2

30. Which of the following has the correct combination considering column I and column II?

(a) Q, 2 (b) P, 3

(c) R, 4

(d) S, 1, 4

(3250)

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# **CHECK YOUR PERFORMANCE**

.....

.....

.....

No. of questions attempted

Marks scored in percentage

If your score is

No. of questions correct

> 80% 60-80% Your preparation is going good, keep it up to get high score.

Need more practice, try hard to score more next time.

<60%

Stress more on concepts and revise thoroughly.





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2020

Unit 2

# **Electrochemistry | Chemical Kinetics | Surface Chemistry**

# Electrochemistry

#### **E**LECTROCHEMISTRY

- Electrochemistry is the study of relationship between electrical energy and chemical energy, produced in a redox reaction, and how one can be converted into another.
- Conductors are substances which allow the passage of current whereas insulators do not allow electric current to pass through them.
- Electrolytes are the aqueous solutions of compounds which conduct electricity and are decomposed to their ions by the passage of current.
- A compound whose aqueous solution does not conduct electricity, is called non-electrolyte.
- Electrolysis is a chemical reaction brought about by the passage of electric current through an electrolyte.
- Electrochemical cell is a device in which the free energy of physical or chemical process is converted into electrical energy.

#### FARADAY'S LAWS OF ELECTROLYSIS

• First law of electrolysis: Amount of substance deposited or liberated at an electrode is directly proportional to amount of charge passed (utilized)

through the electrolyte.

 $W \propto Q$ 

 $W = ZQ = Z \times I \times t$ 

Z = Electrochemical equivalent

• Second law of electrolysis: When same amount of charge is passed through different electrolytic solutions connected in series then mass of substances deposited or dissolved at anode or cathode are in ratio of their equivalent mass. *i.e.*,  $W_1/W_2 = E_1/E_2$ 

#### GALVANIC CELL

This cell converts chemical energy produced in a redox reaction into electrical energy. Galvanic cell is made up of two half cells *i.e.*, anodic and cathodic. Oxidation takes place at anode and reduction at cathode. It is also known as voltaic cell. In this zinc rod act as anode, immersed in ZnSO<sub>4</sub> solution and copper rod act as cathode, immersed in CuSO<sub>4</sub> solution. Two rods are connected by a wire and two solutions are connected by a salt bridge.

• Anode half cell reaction :

 $Zn_{(s)} \rightarrow Zn_{(aq)}^{2+} + 2e^{-}$  (oxidation)

Cathode half cell reaction :

 $Cu_{(aq)}^{2+} + 2e^{-} \rightarrow Cu_{(s)}$  (reduction)

• Overall process:  $Zn_{(s)} + Cu_{(aq)}^{2+} \rightarrow Cu_{(s)} + Zn_{(aq)}^{2+}$ 

In galvanic cell like Daniell cell; electrons flow from anode (zinc rod) to the cathode (copper rod) through external circuit. Zinc dissolves as  $Zn^{2+}$  in solution and  $Cu^{2+}$  ion, in the cathode cell picks up two electron and deposited at copper rod.

- Electrode potential: The electrical potential difference set up between the metal and its ions in the solution is called electrode potential or the tendency of an electrode to lose or gain electrons when it is in contact with solution of its own ions.
- Standard electrode potential: At the unity concentration of electrode and temperature 25°C, the potential of the electrode is termed as standard electrode potential ( $E_{\text{cell}}^{\circ}$ ).

The standard electrode potential of hydrogen electrode is zero. So, it is used as reference electrode.

- Electromotive force (emf): The difference between the electrode potentials of the two half cells is known as cell potential or cell voltage. It is called emf of the cell if no current is drawn from the cell.
- The arrangement of all the electrodes in order of their increasing standard reduction potentials, called electrochemical series.

Reduction potential = -oxidation potential

- Substances with stronger reducing power are placed above hydrogen and those with weaker reducing power are placed below hydrogen.
- Applications of electrochemical series :
  - It is useful in predicting the relative strengths of oxidising and reducing agents.
  - Reactivity of an element can be predicted.
  - It is useful to predict whether a metal will

- liberate hydrogen gas from an acid or not.
- To predict feasibility of a redox reaction by calculating standard EMF of cell:  $E_{\text{cell}}^{\circ} = E_R^{\circ} E_L^{\circ}$

#### NERNST EQUATION

For a reduction reaction,

$$M^{n+}_{(aq)} + ne^{-} \longrightarrow M_{(s)}$$

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{2.303RT}{nF} \log \frac{1}{[M_{(aq)}^{n+}]}$$

At T = 298 K;  $R = 8.314 \text{ J K}^{-1} \text{ mole}^{-1} \text{ and } F = 96500 \text{ C}$ , we get

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log \frac{1}{[M_{(aq)}^{n+}]}$$

For concentration cell,

$$E_{\text{cell}} = \frac{0.0591}{n} \log \frac{C_2}{C_1}$$
; where  $C_2 > C_1$ 

- Applications of Nernst equation :
  - To calculate electrode potential of a cell:

$$aA + bB \xrightarrow{ne^{-}} xX + yY$$

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log \frac{[X]^{x} [Y]^{y}}{[A]^{a} [B]^{b}}$$

To calculate equilibrium constant :

At equilibrium,  $E_{cell} = 0$ 

$$E_{\text{cell}}^{\circ} = \frac{0.0591}{n} \log K_c$$
 at 298 K

Relation between cell potential and Gibbs' energy change:

$$\Delta G^{\circ} = -nFE^{\circ}_{cell}$$
;  $\Delta G^{\circ} = -2.303 \ RT \log K_c$ 

#### SOME COMMERCIAL CELLS

	Dry cell	Lead storage battery	Fuel cell
Anode	Zinc	Lead	Porous carbon containing catalysts (H <sub>2</sub> passed)
Cathode	Graphite	Lead dioxide	Porous carbon containing catalysts (O <sub>2</sub> passed)
Electrolyte	MnO <sub>2</sub> + C (touching cathode) NH <sub>4</sub> Cl + ZnCl <sub>2</sub> (touching anode)	H <sub>2</sub> SO <sub>4</sub> (38%)	Conc. aqueous KOH/NaOH
Anode reaction	$Zn_{(s)} \longrightarrow Zn_{(aq)}^{2+} + 2e^{-}$	$Pb_{(s)} + SO_{4(aq)}^{2-} \longrightarrow PbSO_{4(s)} + 2e^{-}$	$H_{2(g)} + 2OH_{(aq)}^{-} \longrightarrow$ $2H_2O_{(l)} + 2e$
Cathode reaction	$2\text{MnO}_{2(s)} + 2\text{NH}_{4(aq)}^{+} + 2e^{-}$ $\longrightarrow \text{Mn}_{2}\text{O}_{3(s)} + \text{H}_{2}\text{O}_{(l)} + 2\text{NH}_{3(g)}$	$PbO_{2(s)} + SO_{4(aq)}^{2-} + 4H_{(aq)}^{+} + 2e^{-}$ $\implies PbSO_{4(s)} + 2H_{2}O_{(l)}$	$O_{2(g)} + 2H_2O_{(l)} + 4e^-$ $\longrightarrow 4OH_{(aq)}^-$

#### PEEP INTO PREVIOUS YEARS

1. For the cell reaction:

 $2Fe_{(aq)}^{3+} + 2I_{(aq)}^{-} \longrightarrow 2Fe_{(aq)}^{2+} + I_{2(aq)}$ 

 $E^{\circ}_{cell} = 0.24 \text{ V}$  at 298 K. The standard Gibbs' energy  $(\Delta_r G^{\circ})$  of the cell reaction is

[Given that Faraday constant,  $F = 96500 \text{ C mol}^{-1}$ ]

- (a)  $23.16 \text{ kJ mol}^{-1}$  (b)  $-46.32 \text{ kJ mol}^{-1}$
- (c)  $-23.16 \text{ kJ mol}^{-1}$
- (d) 46.32 kJ mol<sup>-1</sup>

(NEET 2019)

2. For the following cell,

 $\operatorname{Zn}_{(s)} | \operatorname{ZnSO}_{4(aq)} | | \operatorname{CuSO}_{4(aq)} | \operatorname{Cu}_{(s)}$ 

when the concentration of Zn<sup>2+</sup> is 10 times the concentration of  $Cu^{2+}$ , the expression for  $\Delta G$ (in  $J \text{ mol}^{-1}$ ) is

[F is Faraday constant; R is gas constant; T is temperature;  $E_{\text{cell}}^{\circ} = 1.1 \text{ V}$ 

- (a) 2.303 RT 2.2F (b) -2.2F
- (c) 2.303 RT + 1.1F
- (d) 1.1*F*

(JEE Advanced 2017)

#### ELECTRICAL RESISTANCE AND CONDUCTANCE

- Ohm's law relates the current, potential difference (E) and the resistance (R) of the conductor as i = E/R.
- The SI unit of electric resistance is ohm  $(\Omega)$ . At a given temperature resistance is directly proportional to length (l) and inversely proportional to area of cross section (a) of the conductor, i.e.,

 $R \propto \frac{l}{a}$  or  $R = \frac{\rho \times l}{a}$ ; where  $\rho$  is specific resistance or resistivity, if *l* and *a* are unity then,  $R = \rho$ 

Conductance (*C*) is the reciprocal of resistance.

$$C = \frac{1}{R}$$

Its unit is ohm<sup>-1</sup> or mho. The SI unit is Siemens (S).

# Specific, Equivalent and Molar Conductivities

Specific Conductance (κ)

Since, 
$$C = \frac{1}{R}$$
 and  $R = \frac{\rho \times l}{a}$   $\therefore$   $C = \frac{1}{\rho} \times \frac{a}{l} = \kappa \frac{a}{l}$ .

к is called specific conductance. Specific conductance of an electrolyte is the conductance of 1 cm<sup>3</sup> solution between electrodes placed 1 cm apart.

$$\therefore \quad \kappa = C \times \frac{l}{a}$$

l/a is called cell constant. Unit of  $\kappa$  is ohm<sup>-1</sup> cm<sup>-1</sup> or mho cm<sup>-1</sup>. The SI unit is S m<sup>-1</sup>.

Equivalent Conductance,  $(\Lambda)$  is more useful comparing the conducting power of different electrolyte solutions, having different concentrations of ions.

If 1 cm<sup>3</sup> solution contains 1 gm equivalent weight of electrolyte then conductance of the solution = equivalent conductance.

If concentration, C is given in gram equivalents per litre, then,

$$V = \frac{1000}{C}$$
 or,  $\Lambda = \kappa \times V = \kappa \times \frac{1000}{C}$ 

C in g- eq/litre = normality Unit of  $\Lambda$  is ohm<sup>-1</sup> m<sup>2</sup> g eq<sup>-1</sup>.

Molar conductance  $(\Lambda_m)$  or molar conductivity is defined as the conducting power of all the ions produced by one mole of electrolyte in the solution.  $\therefore \Lambda_m = \kappa \times V_m$ , where  $V_m = \text{volume of solution}$ 

containing 1 mole of electrolyte. If  $C_m$  is concentration in moles litre<sup>-1</sup> then,

$$\Lambda_m = \kappa \times \frac{1000}{C_m}$$
;  $C_m = \text{molarity}$ 

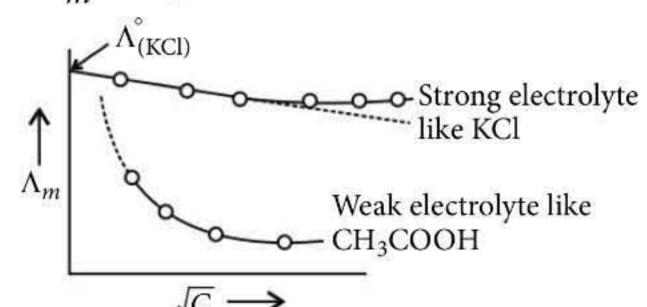
In SI system, concentration  $C_m$  is expressed as moles/m<sup>3</sup> and volume  $V_m$  as m<sup>3</sup> per mole.

$$V_m = \frac{1}{C_m}, :: \Lambda_m = \kappa \times V_m = \frac{\kappa}{C_m}.$$

Unit of  $\Lambda_m$  is ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>, in SI system it is  $ohm^{-1} m^2 mol^{-1}$ .

of Variation molar conductivity with concentration: For a strong electrolyte, Debye-Huckel Onsager equation is as follows:

$$\Lambda_m = \Lambda_m^{\circ} - A\sqrt{C}$$



Here,  $\Lambda_m$ = Molar conductivity at infinite dilution (Limiting molar conductivity)

 $\Lambda_m$  = Molar conductivity at V-dilution

A =Constant which depends upon nature of solvent and temperature

C = Concentration

Plot of  $\Lambda_m$  against  $C^{1/2}$  (for a strong electrolyte) is a straight line with intercept equal to  $\Lambda_m^{\circ}$  and slope equal to '-A'.

Thus,  $\Lambda_m^c$  decreases linearly with  $\sqrt{C}$ , when C = 0,  $\Lambda_m^c = \Lambda_m^o$ .  $\Lambda_m^o$  can be determined experimentally.

#### KOHLRAUSCH'S LAW

"At infinite dilution, when dissociation is complete, each ion makes a definite contribution towards molar conductance of the electrolyte irrespective of the nature of the other ion with which it is associated and that the molar conductance of any electrolyte at infinite dilution is given by the sum of the contributions of the two ions". This is called Kohlrausch's law.

$$\Lambda_m^{\infty} = \lambda_+^{\infty} + \lambda_-^{\infty}$$

 $\lambda_{+}^{\infty}$  and  $\lambda_{-}^{\infty}$  are molar ionic conductances at infinite dilution for cations and anions.

#### Applications of Kohlrausch's Law

It is useful in the calculation of  $\lambda_m^{\infty}$  for weak electrolytes, e.g.,

 $\Lambda_{m\text{CH}_3\text{COOH}}^{\infty} = \Lambda_{m\text{CH}_3\text{COONa}}^{\infty} + \Lambda_{m\text{HCl}}^{\infty} - \Lambda_{m\text{NaCl}}^{\infty}$ 

In the calculation of degree of dissociation, e.g.,

molar conductivity at conc.  $C = \Lambda_m^C$ molar conductivity at infinite dilution  $\Lambda_m^{\infty}$ 

Useful in calculation of solubility of a sparingly soluble salt. The solution of a sparingly soluble salt becomes saturated at infinite dilution, then  $\Lambda_m = \Lambda_m^{\infty}$  and molarity = solubility, hence  $\Lambda_m = \frac{\kappa \times 1000}{\text{molarity}}$ 

or solubility (moles  $L^{-1}$ ) =  $\frac{\kappa \times 1000}{\Lambda_m^{\infty}}$ 

# PEEP INTO PREVIOUS YEARS

Following limiting molar conductivities are given as:

$$\lambda_{m(H_2SO_4)}^{\circ} = x S cm^2 mol^{-1}$$

$$\lambda_{m(K_2SO_4)}^{\circ} = y S cm^2 mol^{-1}$$

$$\lambda_{m(CH_3COOK)}^{\circ} = z \text{ S cm}^2 \text{ mol}^{-1}$$

$$\lambda_m^{\circ}$$
 (in S cm<sup>2</sup> mol<sup>-1</sup>) for CH<sub>3</sub>COOH will be

- (a) x y + 2z (b) x + y z (c) x y + z (d) (x y)/2 + z

(Odisha NEET 2019)

- The molar conductivity of a 0.5 mol/dm<sup>3</sup> solution of AgNO<sub>3</sub> with electrolytic conductivity of  $5.76 \times 10^{-3}$ S cm<sup>-1</sup> at 298 K is

  - (a)  $2.88 \text{ S cm}^2/\text{mol}$  (b)  $11.52 \text{ S cm}^2/\text{mol}$
  - (c)  $0.086 \,\mathrm{S \, cm^2/mol}$  (d)  $28.8 \,\mathrm{S \, cm^2/mol}$

(NEET-II 2016)

# POINTS FOR EXTRA SCORING

- Thermodynamic efficiency  $(\eta)$  of a fuel cell
- $\Delta G_3^{\circ} = \Delta G_1^{\circ} + \Delta G_2^{\circ}$  (when different number of electrons are involved)

$$-n_3FE_3^{\circ} = -n_1FE_1^{\circ} - n_2FE_2^{\circ}$$

$$n_3 E_3^{\circ} = n_1 E_1^{\circ} + n_2 E_2^{\circ} \text{ or } E_3^{\circ} = \frac{n_1 E_1^{\circ} + n_2 E_2^{\circ}}{n_3};$$

if 
$$n_1 = n_2 = n_3$$
,  $E_3^{\circ} = E_1^{\circ} + E_2^{\circ}$ 

$$E_{\text{H}^+/\text{H}_2} = E^{\circ}_{\text{H}^+/\text{H}_2} - 0.0591 \log \frac{1}{[\text{H}^+]}$$

$$= 0 - 0.0591(-\log[H^+]) = -0.0591 \text{ pH}$$

$$\therefore$$
 pH = -log[H<sup>+</sup>]

As pH of the solution increases, electrode potential of hydrogen electrode decreases.

For concentration cell,  $Zn \mid Zn^{2+} \parallel Zn^{2+} \mid Zn$ ;

$$E_{\text{cell}} = \frac{0.0591}{2} \log \left( \frac{C_2}{C_1} \right) (C_2 > C_1)$$

For gas concentration cell,

$$P_1$$
  $P_2$ 

$$P_1$$
  $P_2$ 

$$E_{cell} = 0.0591 \log \frac{P_2}{P_1} (P_2 > P_1)$$

Determination of transport number :

$$t_{\pm}^{\circ} = \frac{\lambda_{\pm}^{\circ}}{\Lambda_{m}^{\circ}} = \frac{\lambda_{\pm}^{\circ}}{\lambda_{+}^{\circ} + \lambda_{-}^{\circ}}$$

where,  $t_{+}^{\circ}$  = Transport number of cation,  $t_{-}^{\circ}$  = Transport number of anion

# **Chemical Kinetics**

- Chemical kinetics is the branch of chemistry which deals with rate and mechanism of chemical reaction.
- The speed with which the reactants are converted into products is called rate of the reaction.
- The rate of reaction is defined as change in the concentration of any one of the reactants or products per unit time.

#### RATE EXPRESSIONS

For a general reaction :  $aA + bB \rightarrow cC + dD$ Rate of disappearance of A = -d[A]/dtRate of disappearance of B = -d[B]/dtRate of appearance of C = d[C]/dtRate of appearance of D = d[D]/dt

The positive sign shows that concentrations of C and D increases with time and the negative sign indicates that concentrations of A and B decrease with time.

Instantaneous rate of reaction:

$$-\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt}$$
Average rate of reaction:

$$-\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t}$$

Units of rate of reaction  $\text{mol } L^{-1} \text{ s}^{-1} \text{ or mol } L^{-1} \text{ min}^{-1} \text{ (concentration time}^{-1}\text{)}.$ For gaseous reactions; atm min<sup>-1</sup> or atm s<sup>-1</sup>

#### **Factors Influencing Rate of a Reaction**

- Concentration: Greater the concentrations of the reactants, faster is the rate of reaction.
- Physical state of reactants: Reactions involving gaseous reactants are faster than reactions containing solid and liquid reactants.
- **Temperature**: The rate of reaction increases with increase of temperature. For most of the reactions, rate of reaction becomes almost double with 10° rise of temperature.
- **Presence of catalyst :** A catalyst generally increases the speed of a reaction.
- Surface area of reactants: For a reaction involving a solid reactant or catalyst, the greater is the surface area, the faster is the reaction.
- Presence of light: Photochemical reactions take place in the presence of light only.

#### RATE LAW

Rate law or rate equation are the mathematical expression which expresses the observed rate of a reaction in terms of the concentration of the reacting species with each term raised to some power, which may or may not be same as the stoichiometric coefficient of that reactant in a balanced chemical equation. e.g.,  $aA + bB \rightarrow \text{product}$ Rate =  $k[A]^a[B]^b$ .

- Rate constant of a reaction is the rate of the reaction when the molar concentration of each of the reactant is unity i.e., [A] = [B] = 1, Rate = k
- Order of the reaction is the sum of exponents of the concentration terms in the rate law.
- Order of reaction can be zero, integer or fractional.
- Certain bimolecular reactions which follow the first order kinetics are called pseudounimolecular reactions.
- The units of rate constant depend upon the order of reaction.
- The units of the rate constant can be remembered by this formula; liter<sup>n-1</sup> mole<sup>1-n</sup> sec<sup>-1</sup> where, n is the order of the reaction.
- Molecularity of a reaction is defined as the number of reacting molecules which collide simultaneously to bring about a chemical reaction.

e.g., 
$$N_2O_5 \rightarrow N_2O_4 + \frac{1}{2}O_2$$
 (Unimolecular)  
 $H_2 + I_2 \rightarrow 2HI$  (Bimolecular)

Difference between Order and Molecularity

	Order	Molecularity
1.	It is an experimental quantity.	It is a theoretical concept.
2.	It is the sum of the powers of the concentration terms in rate law.	It is the number of species which simultaneously collide.
3.	It may have fractional values.	It has only whole number values.
4.	It can be zero.	It cannot be zero.

Half-life of reaction: The time in which the concentration of a reactant is reduced to one half of its initial concentration is called half-life of the reaction.  $t_{1/2} \propto \frac{1}{a^{n-1}}$  where, *n* is the order of the reaction.

# RATE LAW, INTEGRATED RATE EQUATIONS FOR THE REACTIONS OF DIFFERENT ORDERS

Order	Rate law	Integrated rate law	Half-life	Units of rate constant	Graph
0	Rate = $k[A]^0$	$[A]_t = -kt + [A]_0$	$t_{1/2} = [A]_0/2k$	$mol L^{-1} s^{-1}$	[A] $vs\ t$ ; slope = $-k$
1	Rate = $k[A]^1$	$ \ln[A]_t = -kt + \ln[A]_0 $	$t_{1/2} = 0.693/k$	$s^{-1}$	ln[A] <i>vs t</i> ; $slope = -k$
2	Rate = $k[A]^2$	$1/[A]_t = kt + 1/[A]_0$	$t_{1/2} = 1/k [A]_0$	$L \text{ mol}^{-1} \text{ s}^{-1}$	1/[A] vs t; slope = k

2	Rate = $k[A][B]$	$kt = \frac{1}{[A]_0 - [B]_0} \ln \frac{[B]_0 [A]}{[A]_0 [B]}$	-	$L \text{ mol}^{-1} \text{ s}^{-1}$	1/[A] vs t; slope = $k$
n	Rate = $k[A]^n$	$(n-1)kt = \frac{1}{[A]^{n-1}} - \frac{1}{[A_0]^{n-1}}$	$t_{1/2} = \frac{2^{n-1} - 1}{k(n-1) [A]_0^{n-1}}$	$(\text{mol L}^{-1})^{1-n}  s^{-1}$	$\frac{1}{[A]^{n-1}} \text{ vs } t; \text{ slope} = (n-1) k$

# PEEP INTO PREVIOUS YEARS

- If the rate constant for a first order reaction is *k*, the time (*t*) required for the completion of 99% of the reaction is given by
  - (a) t = 2.303/k
- (b) t = 0.693/k
- (c) t = 6.909/k
- (d) t = 4.606/k

(NEET 2019)

- The reaction  $2X \rightarrow B$  is a zeroth order reaction. If the initial concentration of X is 0.2 M, the half-life is 6 h. When the initial concentration of *X* is 0.5 M the time required to reach its final concentration of 0.2 M will be
  - (a) 12.0 h (b) 9.0 h (c) 7.2 h
- (d) 18.0 h

(JEE Main 2019)



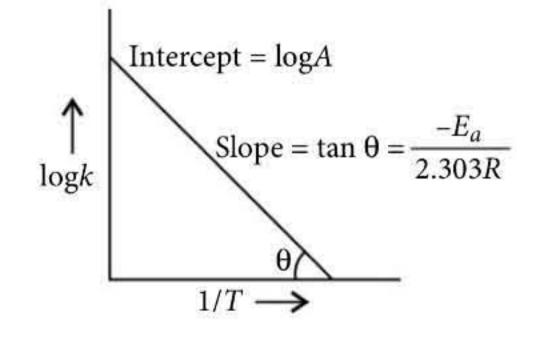
The effect of temperature on the rate of reaction and hence on the rate constant k, was proposed by Arrhenius, which is known as Arrhenius equation.

$$k = Ae^{-Ea/RT}$$

where, k = Rate constant, A = Pre-exponential factor, T = Temperature in kelvin,  $E_a =$  Activation Energy The factor  $e^{-Ea/RT}$  represents fraction of molecules that have kinetic energy greater than  $E_a$ .

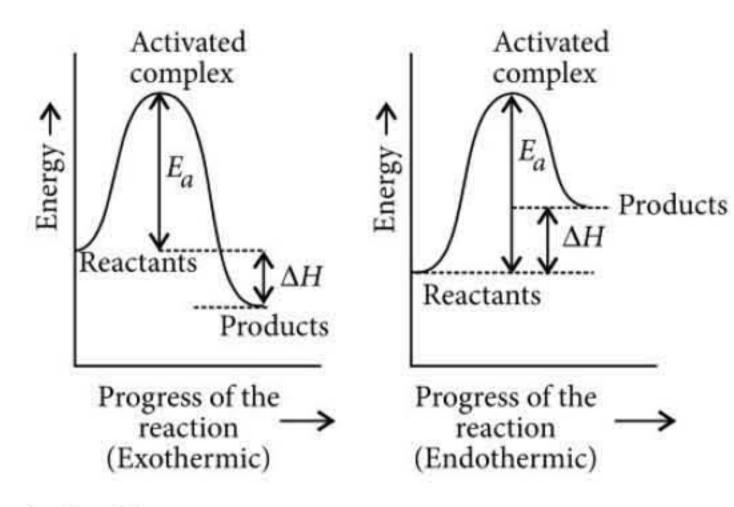
# **Logarithmic Expression**

$$\log_{10}\left(\frac{k_2}{k_1}\right) = \frac{E_a}{2.303 R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$



#### ACTIVATION ENERGY

The minimum amount of energy required by reactant molecules to participate in a reaction is called activation energy ( $E_a$ ).



- Activation energy = Threshold energy - Average kinetic energy of reacting molecules
- Activation energy  $(E_a)$

 $= E_{\text{(activated complex)}} - E_{\text{(ground state)}}$ 

 $\Delta H$  = Activation energy of forward reaction – Activation energy of backward reaction

#### COLLISION THEORY

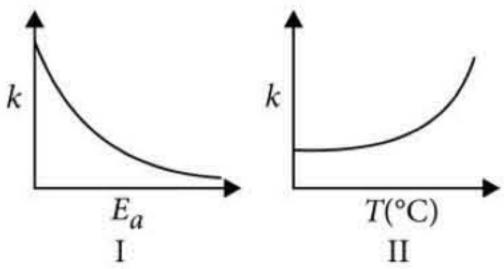
According to this theory rate of reaction depends upon the number of effective collisions which in turn depends upon energy factor and orientation factor.

 $k = PZ_{AB} e^{-E_a/RT}$ 

P = Probability or orientation factor

# PEEP INTO PREVIOUS YEARS

Consider the given plots for a reaction obeying Arrhenius equation (0°C < T < 300°C) : (k and  $E_a$ are rate constant and activation energy, respectively)



Choose the correct option.

- (a) I is right but II is wrong.
- (b) Both I and II are wrong.
- (c) I is wrong but II is right.
- (d) Both I and II are correct. (JEE Main 2019)

- **8.** In a bimolecular reaction, the steric factor *P* was experimentally determined to be 4.5. The correct option(s) among the following is(are)
  - (a) experimentally determined value of frequency factor is higher than that predicted by Arrhenius equation
  - (b) the value of frequency factor predicted by Arrhenius equation is higher than that determined experimentally
  - (c) the activation energy of the reaction is unaffected by the value of the steric factor
  - (d) since P = 4.5, the reaction will not proceed unless an effective catalyst is used.

(JEE Advanced 2017)

# POINTS FOR EXTRA SCORING

For a reversible reaction at equilibrium,

$$\left(\frac{dx}{dt}\right)_{\text{forward}} = \left(\frac{dx}{dt}\right)_{\text{backward}}$$

The overall rate of reaction,

$$\frac{dx}{dt} = \left(\frac{dx}{dt}\right)_{\text{forward}} - \left(\frac{dx}{dt}\right)_{\text{backward}} = 0$$

Some useful relationships between time periods for different fractions of reaction of first order to complete.

$$t_{3/4}$$
 or  $t_{75\%} = 2t_{1/2}$ ,  $t_{87.5\%} = 3t_{1/2}$ ,  $t_{93.75\%} = 4t_{1/2}$ ,  $t_{96.87\%} = 5t_{1/2}$ ,  $t_{99.9\%} = 10t_{1/2}$ 

General expression for time taken for  $n^{th}$  fraction of a reaction of 1st order to complete

(by putting 
$$x = \frac{a}{n}$$
,  $t = t_{1/n}$ );  $t_{1/n} = \frac{2.303}{k} \log \frac{n}{n-1}$ 

Average life ( $\tau$ ) is taken as the reciprocal of the disintegration constant (k), i.e.,  $\tau = \frac{1}{k} = \frac{t_{1/2}}{0.693} = 1.44 \times t_{1/2}$ 

Amount of the substance left after 'n' half-lives  $= \frac{[A]_0}{2^n}$ 

# **Surface Chemistry**

#### **ADSORPTION**

- Adsorption is the phenomenon of attracting and retaining the molecules of a substance on the surface of a liquid or solid, resulting in a higher concentration of molecules on the surface.
- Adsorption is a surface phenomenon.
- The substance being adsorbed is called adsorbate and the substance on whose surface it is being adsorbed is called the adsorbent.
- Sorption is a term used when both absorption and adsorption occur simultaneously.
- Desorption is the reverse of adsorption, i.e., the removal of the adsorbed substance from the surface of the adsorbent.
- Occlusion is a term used for adsorption of gases on a metal surface.
- Adsorption is specific and selective in nature.

# **Type of Adsorption**

- Based on Concentration :
  - Positive adsorption: If the concentration of adsorbate is more at the surface as compared

- to its concentration in the bulk phase then it is called positive adsorption.
- Negative adsorption: If concentration of adsorbate is less at the surface as compared to its concentration in the bulk phase then it is called negative adsorption.
- Based on forces existing between adsorbate molecule and adsorbent:
  - Physical adsorption: If the forces of attraction existing between adsorbate and adsorbent are van der Waals' forces, then adsorption is called physical adsorption.
  - Chemical adsorption: If the forces of attraction existing between adsorbate particles and adsorbent are almost of the same strength as chemical bonds then adsorption is called chemical adsorption.

# Quotable Quote 99

"An experiment is a question which science poses to Nature, and a measurement is the recording of Nature's answer."

**MAX PLANCK** 

#### **Differences** Physisorption between and **Chemisorption:**

Property	Physisorption	Chemisorption	
Enthalpy	Low enthalpy, in the order of 20-40 kJ mol <sup>-1</sup> .	High enthalpy, in the order of 80-240 kJ mol <sup>-1</sup> .	
Reversibility	Reversible process	Irreversible process	
Effect of temperature	With the increase in temperature, extent of adsorption decreases because adsorption is a exothermic process and kinetic energy of gas molecules increases with temperature.	Chemisorption first increases with temperature upto a certain extent and then decreases. A gas adsorbed at low temperature by physical adsorption may change into chemisorption at high temperature.	
Selectivity	Not selective in nature.	Highly selective in nature.	
Nature and state of adsorbate	The extent of adsorption depends upon the ease of liquefaction of the gas.	The state of adsorbed molecules may be different from that in the bulk.	
Activation energy	No appreciable energy needed.	High activation energy needed.	
Pressure	Increase in pressure increases adsorption.	Increase in pressure decreases adsorption.	
Layers	Multimolecular layer.	Mono-molecular layer.	

#### ADSORPTION ISOTHERM

Graph between extent of the adsorption  $\left(\frac{x}{x}\right)$ and

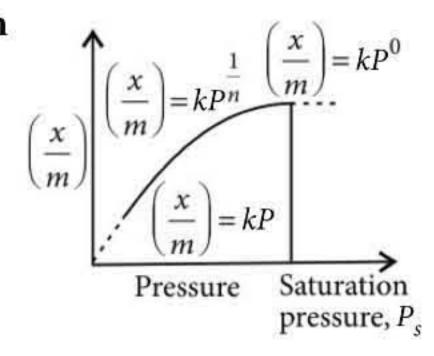
pressure (*P*) at a given temperature is called adsorption isotherm. There are two types of adsorption isotherms:

#### Freundlich Adsorption **Isotherm**:

Freundlich's Equation,

$$\frac{x}{m} = k \times P^{1/n}$$

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log P$$

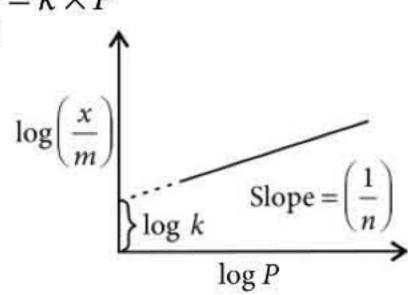


where x = mass of adsorbate adsorbed, m =mass of adsorbent, P =pressure

- At low pressure:  $\frac{x}{-} = k \times P$
- At intermediate pressure:

$$\frac{x}{m} = k \times P^{1/n} ,$$

Where,  $n \ge 1$ 

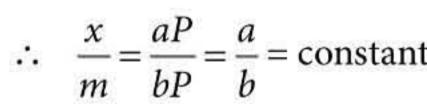


- At high pressure : x/m = constant
- Langmuir Adsorption Isotherm : Assuming adsorption to be unimolecular, Langmuir deduced a relationship theoretically:

$$\frac{x}{m} = \frac{aP}{1 + bP}$$

Where, a and b Langmuir parameters which depends upon the nature of the gas adsorbate, the nature of solid adsorbent and the temperature.

Case-I: At very high pressure bP >>> 1,



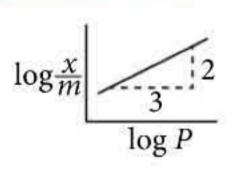
P -0

Case-II: At very low pressure bP <<< 1

$$\therefore \quad \frac{x}{m} = aP$$

# PEEP INTO PREVIOUS YEARS

Adsorption of a gas follows Freundlich adsorption isotherm. x is the mass of the gas adsorbed on mass m of the adsorbent.



The plot of  $\log \frac{x}{m}$  versus  $\log P$  is shown in the given

graph.  $\frac{x}{m}$  is proportional to

(a)  $P^2$ 

- (c)  $P^{2/3}$
- (b)  $P^3$  (d)  $P^{3/2}$  (JEE Main 2019)
- 10. Methylene blue, from its aqueous solution, is adsorbed on activated charcoal at 25°C. For this process, the correct statement is
  - (a) the adsorption requires activation at 25°C
  - the adsorption is accompanied by a decrease in enthalpy
  - the adsorption increases with increase of temperature
  - (d) the adsorption is irreversible.

(JEE Advanced 2013)

#### CATALYST

**Catalysis**: Substances which accelerate the rate of a chemical reaction and themselves remain chemically and quantitatively unchanged after the reaction, are known as *catalysts*, and the phenomenon is known as *catalysis*.

#### **Homogeneous Catalysis**

The process in which the reactants and the catalyst are in the same phase.

e.g., oxidation of SO<sub>2</sub> to SO<sub>3</sub> by NO as catalyst (lead chamber process), hydrolysis of methyl acetate by HCl, hydrolysis of sugar by H<sub>2</sub>SO<sub>4</sub>.

#### Heterogeneous Catalysis

The process in which the reactants and the catalyst are in different phases. e.g., oxidation of SO<sub>2</sub> to SO<sub>3</sub> by Pt, manufacture of NH<sub>3</sub> from N<sub>2</sub> and H<sub>2</sub> by Fe (Haber's process), oxidation of NH<sub>3</sub> to NO by Pt (Ostwald's process), hydrogenation of vegetable oils by Ni.

 Activity of a catalyst refers to the ability of a catalyst to accelerate chemical reaction.
 e.g., Pt acts as a catalyst in the reaction,

$$H_{2(g)} + 1/2 O_{2(g)} \xrightarrow{\text{platinum}} H_2 O_{(l)}$$

- Selectivity of a catalyst refers to the ability of a catalyst to direct a reaction to yield a particular product (excluding others), e.g., n-heptane selectively gives toluene in presence of platinum as catalyst.
- Some enzymatic reactions :

	Enzyme	Source	Enzymatic reaction
1.	Invertase	Yeast	Sucrose → glucose and fructose
2.	Zymase	Yeast	Glucose → ethyl alcohol and carbon dioxide
3.	Diastase	Malt	Starch → maltose
4.	Maltase	Yeast	Maltose → glucose
5.	Urease	Soyabean	Urea → ammonia and carbon dioxide.

#### Shape-selective Catalysis

The catalytic reaction that depends upon the pore structure of the catalyst and the size of the reactant and product molecules. *e.g.*, Zeolites,  $M_{x/n}[(AlO_2)_z (SiO_2)_y] \cdot mH_2O$ , having honeycomb like structures.

#### **Enzyme Catalysis**

Many biochemical reactions are catalysed by complex nitrogeneous organic compounds (proteins or enzymes) which are also called biochemical catalysts and the phenomenon is known as biochemical catalysis.

#### PEEP INTO PREVIOUS YEARS

- 11. Which of the following is not an example of heterogeneous catalytic reaction?
  - (a) Haber's process
  - (b) Hydrogenation of vegetable oils
  - (c) Combustion of coal
  - (d) Ostwald's process

(JEE Main 2019)

- 12. Which one of the following statements is not correct?
  - (a) The value of equilibrium constant is changed in the presence of a catalyst in the reaction at equilibrium.
  - (b) Enzymes catalyse mainly biochemical reactions.
  - (c) Coenzymes increase the catalytic activity of enzyme.
  - (d) Catalyst does not initiate any reaction.

(NEET 2017)

#### COLLOIDAL STATE

 Colloidal state of matter is a state in which the size of the particles (1 to 1000 nm) is such that they can pass through filter paper but not through animal or vegetable membrane.

#### **Classification of Colloids**

Based on physical state of dispersed phase and dispersion medium :

- Sols : Solids in liquids
   e.g., paints
- Gels: Liquids in solids e.g., cheese
- Emulsions : Liquids in liquids.
  - Oil in water type emulsions *e.g.*, milk.
  - Water in oil type emulsions e.g., butter.

Based on nature of interaction between dispersed phase and dispersion medium:

- Lyophilic colloids: Liquidloving, directly formed, reversible in nature, quite stable, cannot be easily coagulated.
- Lyophobic colloids: Liquidhating, prepared by special methods, readily coagulated, irreversible, not stable, and need stabilising agents for their preservation.

Based on type of particles of the dispersed phase:

#### Multimolecular colloids

Formed by aggregation of a large number of atoms or molecules (diameter < 1 nm) held by weak van der Waals forces.

#### Macromolecular colloids

Formed by molecules of large size.

#### Associated colloids

Formed by substance which at low concentrations behave as strong electrolytes, but at higher concentrations exhibit colloidal behaviour due to the formation of aggregates (called micelles).

#### **Preparation of Colloids**

Lyophobic sols are prepared indirectly by any of the following methods:

#### Dispersion or Disintegration Methods

- Electro-dispersion by Bredig's arc method is used to prepare sols of metals like Ag, Cu, Au, Pt etc. A direct current is passed through electrodes of the metal, the electric arc vapourizes the metal and vapours condense in the medium to form a sol.
- Peptization involves the conversion of a freshly prepared precipitate into colloidal size particles by shaking with a suitable electrolyte, e.g., freshly prepared Fe(OH)<sub>3</sub> is treated with FeCl<sub>3</sub> or AgI with AgNO<sub>3</sub> etc. The electrolyte used is called a peptizing agent.

#### Condensation or Aggregation Methods

- These methods involve the joining together smaller particles to form colloidal size particles.
- Chemical methods involve different chemical reactions yielding a sol, e.g.,

#### Double decomposition :

$$As_2O_{3(aq)} + 3H_2S_{(aq)} \rightarrow As_2S_3 + 3H_2O$$

#### **Reduction:**

$$2\text{AuCl}_{3(aq)} + 3 \text{SnCl}_{2(aq)} \rightarrow 2\text{Au} + 3\text{SnCl}_{4}$$

**Oxidation**: 
$$Br_{2(aq)} + H_2S_{(aq)} \rightarrow S + 2HBr$$

**Hydrolysis :** 
$$FeCl_{3(aq)} + 3H_2O \rightarrow Fe(OH)_3 + 3HCl$$
 sol

• Exchange of solvent is the method used to prepare sols of substances less soluble in water, e.g., water is added to a solution of sulphur or phosphorus in alcohol to yield a sol.

#### **Properties of Colloidal Solutions**

 Colligative properties: Colloids show colligative properties like relative lowering of vapour pressure, elevation of boiling point, etc. and magnitude of colligative properties of colloids is much less than true solutions due to larger size of colloidal particles.

M	onthly	Test	Drive	CLA	SS XI	A	NSN	/ER	KEY
1.	(a)	2.	(a)	3.	(b)	4.	(b)	5.	(d)
6.	(b)	7.	(d)	8.	(c)	9.	(c)	10.	(a)
11.	(d)	12.	(a)	13.	(a)	14.	(d)	15.	(b)
16.	(b)	17.	(d)	18.	(c)	19.	(a)	20.	(b,d)
21.	(b,c)	22.	(a,b,c)	23.	(b,c,d)	24.	(6)	25.	(4)
26.	(5)	27.	(d)	28.	(a)	29.	(c)	30.	(b)

- Tyndall effect (Optical property): Scattering of light by colloidal particles due to which the path of light beam becomes visible.
- Brownian movement (Mechanical property) : Zig-zag movement of colloidal particles due to the unbalanced bombardment by the molecules of dispersion medium.
- Charge on colloidal particles: Colloidal particles always carry an electric charge and nature of charge (+ve or -ve) is same on all the particles in a given colloidal solution. The charge is due to preferential adsorption of ions from solution.
- Electrophoresis (Electrical property): Movement of colloidal particles towards one of the electrodes on passage of electricity through colloidal solution. The direction depends on the type of charge on colloidal particles.

#### Coagulation

The stability of the colloidal system is due to the existence of charged particles. If the charges are neutralised or destroyed, then the colloidal solution gets precipitated. This is called Coagulation or Flocculation. It can be done by

- adding electrolyte
- mutual action of sols
- persistent dialysis
- by cooling
- by electrophoresis.
- Coagulation value: The minimum concentration of the electrolyte required in millimoles per litre of solution to cause coagulation or flocculation is called coagulation value.
- Hardy—Schulze rule: According to this rule the coagulating power of the active ion increases with the valency of the active ion.
- Gold number: It is defined as the minimum amount of the protective colloid in milligrams which must be added to 10 mL solution of standard gold sol, which prevents coagulation on adding one mL of 10% NaCl solution.

#### PEEP INTO PREVIOUS YEARS

- 13. The correct option among the following is
  - (a) colloidal particles in lyophobic sols can be precipitated by electrophoresis
  - (b) colloidal medicines are more effective because they have small surface area
  - addition of alum to water makes it unfit for drinking
  - (d) Brownian motion in colloidal solution is faster if the viscosity of the solution is very high.

(JEE Main 2019)

- 14. On which of the following properties does the coagulating power of an ion depend?
  - The magnitude of the charge on the ion alone.
  - Size of the ion alone.
  - Both magnitude and sign of the charge on the ion.
  - (d) The sign of charge on the ion alone.

(NEET 2018)

#### POINTS FOR EXTRA SCORING

- Colloidal antimony is used in curing Kala-azar.
- Argyrol is a silver sol used as eye lotion.
- Colloidal solution of gold in water is called 'Purple of cassius'.
- Catalyst lowers the activation energy and does not change the value of equilibrium constant but helps in attaining the equilibrium faster.
- The graphs plotted T vs P for given amount of adsorption are known as adsorption isostere.
- The flocculation of an emulsion, viz. the formation of aggregates, may be followed by coalescence. If coalescence is extensive it leads to the formation of a macrophase and the emulsion is said to break.
- The deltas at the mouths of great rivers are formed by the precipitation of the charged clay particles carried in suspension in the river water, by the action of salts present in sea-water.
- Blood is a colloidal system of an albuminoid substance.

#### **Answer Key For Peep Into Previous Years**

- (b) (a) (d)
- **(b)**
- 5.
- (d) (a)

- 13.
- (d) (a)
- 8. 14.
- 9.
- (c)
- **(b)**





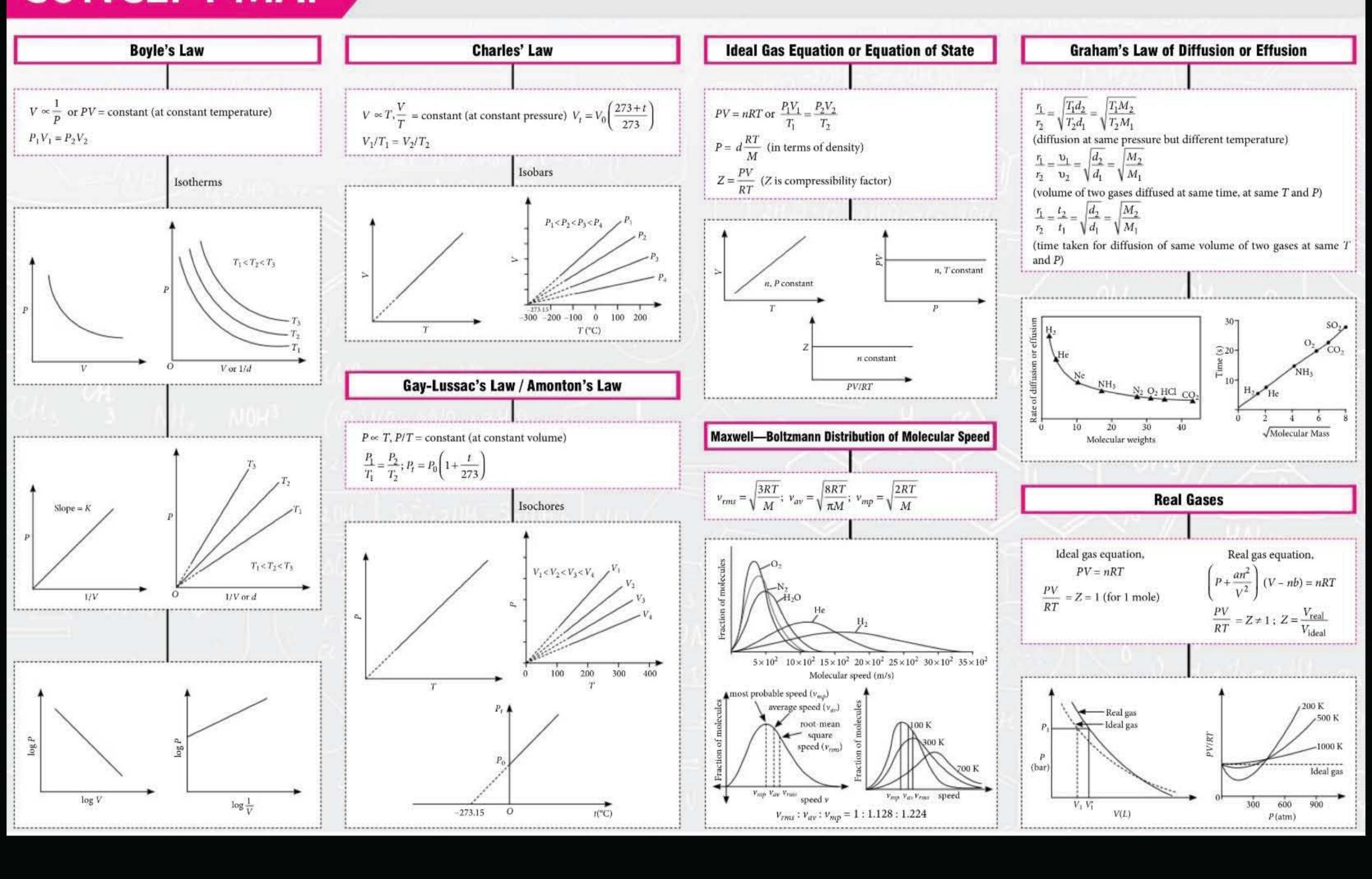


11.

(c)

## CONCEPT MAP

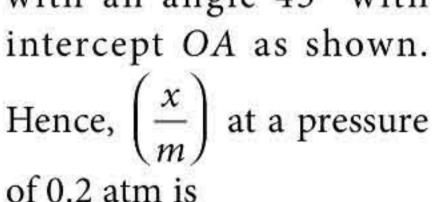
### GRAPHICAL REPRESENTATION OF GASEOUS LAWS



## WRAPitUP

- 1. A certain zeroth order reaction has  $k = 0.025 \text{ M s}^{-1}$ for the disappearance of A. What will be the concentration of A after 15 s if the initial concentration is 0.50 M?
  - (a) 0.50 M (b) 0.375 M (c) 0.125 M (d) 0.060 M
- Four moles of electrons were transferred from anode to cathode in an experiment during electrolysis of water. The total volume of the two gases (dry and at STP) produced will be approximately (in litres) (b) 44.8 (c) 67.2 (a) 22.4 (d) 89.4
- Equivalent conductance of BaCl<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub> and HCl are  $x_1$ ,  $x_2$  and  $x_3$  S cm<sup>2</sup> equiv<sup>-1</sup> at infinite dilution. If specific conductance of saturated BaSO<sub>4</sub> solution is  $y \text{ S cm}^{-1}$ , then  $K_{sp}$  of BaSO<sub>4</sub> is
- (a)  $\frac{10^3 y}{2(x_1 + x_2 2x_3)}$  (b)  $\frac{10^6 y^2}{(x_1 + x_2 2x_3)^2}$ (c)  $\frac{10^6 y^2}{4(x_1 + x_2 2x_3)^2}$  (d)  $\frac{x_1 + x_2 2x_3}{10^6 y^2}$
- 4. Graph between  $\log\left(\frac{x}{m}\right)$ and log p is a straight line with an angle 45° with

Hence,  $\left(\frac{x}{m}\right)$  at a pressure of 0.2 atm is



(a) 0.2

- (b) 0.4
- (c) 0.6
- (d) 0.8

0.3010

- 96500 coulomb deposits 107.8 g of silver. If electronic charge is  $1.6 \times 10^{-19}$  C, value of Avogadro's number is
  - (a)  $6.03 \times 10^{-23} \text{ mol}^{-1}$  (b)  $6.03 \times 10^{23} \text{ mol}^{-1}$

  - (c)  $6.03 \times 10^{19} \text{ mol}^{-1}$  (d)  $6.03 \times 10^{-19} \text{ mol}^{-1}$
- The value of pre-exponential factor (A) is, when  $T \rightarrow \infty$  [Given: Rate constant  $k = 1.2 \times 10^3 \text{ mol}^{-1} \text{ L s}^{-1}$ and  $E_a = 2.0 \times 10^2 \text{ kJ mol}^{-1}$ .
  - (a)  $2.0 \times 10^2 \text{ kJ mol}^{-1}$  (b)  $1.2 \times 10^3 \text{ mol}^{-1} \text{ L s}^{-1}$
  - (c)  $1.2 \times 10^3 \text{ mol L}^{-1} \text{ s}^{-1}$  (d)  $2.4 \times 10^3 \text{ kJ mol}^{-1} \text{ s}^{-1}$
- 1.08 g of pure silver was converted into silver nitrate and its solution was taken in a beaker. It was electrolysed using platinum cathode and silver

anode. 0.01 Faraday of electricity was passed using 0.15 volt above the decomposition potential of silver. The silver content of the beaker after the above process shall be

(a) 0 g

- (b) 0.108 g (c) 0.54 g (d) 1.08 g
- Which of the following are suspensions?

II. Air Fog

- Bone marrow
- (b) Only III, IV and V

III. Blood IV. Paint

(c) Only I, III and V

(a) Only I, II and III

- (d) Only I, II and V
- For the given cell,

 $Pt(H_2)|0.01 \text{ M H}^+|0.1 \text{ M H}^+|Pt(H_2)$ x atm

If  $E_{\text{cell}} = 0.00 \text{ V then } \frac{x}{y}$  is

(a) 100 (b) 10 (c)

- (c) 0.01
- (d) 0.1
- 10. The decomposition of a substance 'R' takes place according to first order kinetics. Its initial concentration is reduced to  $\frac{1}{9}$ th in 24 s. The rate constant of the reaction is

- 11. An example of autocatalysis is
  - (a) oxidation of NO to NO<sub>2</sub>
  - (b) oxidation of SO<sub>2</sub> to SO<sub>3</sub>
  - (c) decomposition of KClO<sub>3</sub> to KCl and O<sub>2</sub>
  - (d) oxidation of oxalic acid by acidified KMnO<sub>4</sub>.
- 12. Consider the following half-cell reactions:

 $H_2O_2 \longrightarrow O_2 + 2H^+ + 2e^-$ ;  $E^0 = -0.69 \text{ V}$  $H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O$ ;  $E^\circ = 1.77 \text{ V}$  $Fe^{2+} \longrightarrow Fe^{3+} + e^{-}$ ;  $E^{\circ} = 0.771 \text{ V}$ 

Fe  $\longrightarrow$  Fe<sup>2+</sup> + 2e<sup>-</sup>;  $E^{\circ} = 0.44 \text{ V}$ 

If H<sub>2</sub>O<sub>2</sub> is mixed with Fe<sup>2+</sup>, which reaction is more likely to occur?

- (a) Oxidation of Fe<sup>2+</sup> to Fe<sup>3+</sup>
- (b) Reduction of Fe<sup>2+</sup> to Fe
- (c) Both (a) and (b)
- (d) None of these

- 13. A G.M. counter is used to study the radioactive process of first order reaction. In the absence of radioactive substance A, it counts 3 disintegration per second (dps). When A is placed in the G.M. counter, it records 23 dps at the start and 13 dps after 10 min. It records x dps after next 10 min and A has half-life period y min. x and y are
  - (a) 8 dps, 10 min
- (b) 5 dps, 10 min
- (c) 5 dps, 20 min
- (d) 5 dps, 5 min.
- 14. Chromatography is a technique based on
  - (a) adsorption and then dispersion of solute
  - (b) absorption of solute
  - (c) hydration of solute
  - (d) evaporation of solute.
- 15. The coagulating power of an electrolyte for arsenious sulphide decreases in the order
  - (a)  $Na^{+} > Al^{3+} > Ba^{2+}$  (b)  $PO_4^{3-} > SO_4^{2-} > Cl^{-}$
- - (c)  $Cl^- > SO_4^{2-} > PO_4^{3-}$  (d)  $Al^{3+} > Ba^{2+} > Na^+$
- 16. The decomposition of  $N_2O$  into  $N_2$  and  $O_2$  in the presence of gaseous argon follows second order kinetics with rate constant,

 $k = (5.0 \times 10^{11} \text{ L mol}^{-1} \text{ s}^{-1}) e^{-29000/T}$ 

Hence,  $E_a$  (energy of activation) is

- (a)  $5.0 \times 10^{11}$  kcal
- (b) 29000 kcal
- (c) 58 kcal
- (d) -29000 cal
- 17. 18 g water is to be decomposed by electrolysis into  $H_2$  and  $O_2$  by a current of 3 A. Time required is approximately
  - (a) 17.87 h
- (b) 35.94 h
- (c) 8.94 h
- (d) 26.80 h
- 18. Match List I (names of the processes) with List II (for the catalysts used).

	List I		List II
I.	Ostwald	P.	Ni
II.	Hydrocarbon re-forming	Q.	NO
III.	Fischer-Tropsch	R.	Pt
IV.	Lead-chamber	S.	Co/Al <sub>2</sub> O <sub>3</sub>

Choose the correct option.

- (a) I-P II-Q III-R IV-S
- (b) I-R II-P III-S
- (c) I-R II-P III-Q
- (d) I-P II-R III-Q IV-S
- 19. The following data is obtained during the first order thermal decomposition of

$$2A_{(g)} \longrightarrow B_{(g)} + C_{(s)}$$

at constant volume and temperature.

S. No.	Time	Total pressure (in pascals)
1.	At the end of 10 minutes	300
2.	After completion	200

The rate constant (in min<sup>-1</sup>) is

- (a) 0.0693 (b) 6.93
- (c) 0.00693 (d) 69.3
- **20.** Peptisation is
  - (a) conversion of colloidal into precipitate form
  - conversion of precipitate into colloidal sol
  - conversion of metal into colloidal sol by passage of electric current
  - (d) conversion of colloidal sol into macromolecules.

#### SOLUTIONS

1. (c): For a zero order reaction,  $\frac{x}{t} = k = 0.025 \,\mathrm{M \, s}^{-1}$ 

$$x = 15 \times 0.025 = 0.375 \text{ M}$$

Thus, [A] = 0.50 - 0.375 = 0.125 M

2. (c): 
$$H_2O \longrightarrow H_2 + \frac{1}{2}O_2$$
  
 $2H^+ + 2e^- \longrightarrow H_2$ 

i.e., 2 moles of e produce 1 mole of H<sub>2</sub>, i.e., 22.4 L Hence, 4 moles of  $e^-$  will give  $H_2 = 44.8 L$ 

$$O_2$$
 produced =  $\frac{1}{2}$  of  $H_2$  = 22.4 L

Total volume = 44.8 + 22.4 = 67.2 L

3. (c): 
$$\Lambda_{\text{BaSO}_4}^{\circ} = \Lambda_{\text{BaCl}_2}^{\circ} + \Lambda_{\text{H}_2\text{SO}_4}^{\circ} - 2\Lambda_{\text{HCl}}^{\circ}$$
  
=  $(x_1 + x_2 - 2x_3)$ 

$$\Lambda_{\text{BaSO}_4}^{\circ} = \frac{1000 \times \text{sp. conductance}}{\text{Normality (or Solubility in g-eq L}^{-1})}$$

$$(x_1 + x_2 - 2x_3) = \frac{1000 \times y}{\text{solubility (in g-eq L}^{-1})}$$

:. Solubility (in g eq L<sup>-1</sup>) = 
$$\frac{1000 y}{(x_1 + x_2 - 2x_3)}$$

Solubility (S) (in mol L<sup>-1</sup>) = 
$$\frac{1000 y}{2(x_1 + x_2 - 2x_3)}$$

BaSO<sub>4</sub> 
$$\rightleftharpoons$$
 Ba<sup>2+</sup> + SO<sub>4</sub><sup>2-</sup>  
 $K_{sp}(BaSO_4) = [Ba^{2+}][SO_4^{2-}] = S^2$ 

$$= \left[ \frac{1000 y}{2(x_1 + x_2 - 2x_3)} \right]^2 = \frac{10^6 y^2}{4(x_1 + x_2 - 2x_3)^2}$$

4. **(b)**: 
$$\log\left(\frac{x}{m}\right) = \log k + \frac{1}{n}\log p$$

Given,  $\log k = 0.3010 = \text{intercept on } y\text{-axis}$ 

and 
$$\frac{1}{n} = \tan 45^\circ = 1$$
 (slope)

$$\log\left(\frac{x}{m}\right) = 0.3010 + 1\log 0.2 = \log 2 + \log 0.2$$

$$\therefore \left(\frac{x}{m}\right) = 0.4$$

5. **(b)**: Number of moles of Ag = 
$$\frac{107.8}{107.8}$$
 = 1

Number of Ag atoms =  $1 \times N_0$  (where,  $N_0$  is the Avogadro's number)

Total charge =  $N_0 \times 1.6 \times 10^{-19}$  C

 $N_0 \times 1.6 \times 10^{-19} = 96500$  (charge carried by 1 mole of electrons)

$$\therefore N_0 = \frac{96500}{1.6 \times 10^{-19}} = 6.03 \times 10^{23} \text{ mol}^{-1}$$

**6. (b)**: 
$$k = Ae^{-E_a/RT}$$

when,  $T \rightarrow \infty$ 

$$\therefore k = Ae^0 = A$$

$$A = k = 1.2 \times 10^3 \text{ mol}^{-1} \text{ L s}^{-1}$$

7. (a): 
$$Ag^+ + e^- \longrightarrow Ag$$
, *i.e.*, 1 F deposits  $Ag = 108 g$ 

$$\therefore$$
 0.01 F will deposit Ag = 1.08 g

Hence, Ag content left = 0

8. (b)

9. (c): LHS: 
$$H_{2(g)} \rightleftharpoons 2H_{(aq)}^+ + 2e^-$$

RHS: 
$$2H_{(aq)}^{+} + 2e^{-} \rightleftharpoons H_{2(g)}$$
  
 $0.1 \text{ M}$   $y \text{ atm}$   
 $H_{2(g)} + 2H_{(aq)}^{+} \rightleftharpoons 2H_{(aq)}^{+} + H_{2(g)}$   
 $x \text{ atm}$   $0.1 \text{ M}$   $0.01 \text{ M}$   $y \text{ atm}$ 

$$K = \frac{(0.01)^2 y}{(0.1)^2 x} = 0.01 \left(\frac{y}{x}\right)$$

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{2} \log (0.01) \left(\frac{y}{x}\right)$$

$$0 = 0 + 0.0591 \log 10 - \frac{0.0591}{2} \log \frac{y}{x}$$

$$\log 10 = \log \left(\frac{y}{x}\right)^{1/2} \quad \therefore \quad 10 = \left(\frac{y}{x}\right)^{1/2}$$

$$\left(\frac{x}{y}\right)^{1/2} = \frac{1}{10} \quad \therefore \quad \frac{x}{y} = 0.01$$

10. (c): For first order reaction, 
$$k = \frac{1}{t} \ln \frac{a}{(a-x)}$$

$$k = \frac{1}{24} \ln \frac{a}{a/8} = \frac{1}{24} \ln 8 = \frac{1}{24} \ln 2^3 = \frac{1}{8} \ln 2 \text{ s}^{-1}$$

11. (d): 
$$2KMnO_4 + 3H_2SO_4 + 5H_2C_2O_4$$

$$\longrightarrow$$
 K<sub>2</sub>SO<sub>4</sub> + 2MnSO<sub>4</sub> + 8H<sub>2</sub>O + 10CO<sub>2</sub>

Mn<sup>2+</sup> ions produced in the reaction act as autocatalyst.

12. (a): 
$$H_2O_2 + 2H^+ + 2Fe^{2+} \longrightarrow 2Fe^{3+} + 2H_2O$$
  
 $E_{cell}^o = 1.77 + 0.771 = 2.541 \text{ V}$ 

13. (a): There is an error of 3 dps

$$\therefore$$
  $C_0 = 20 \text{ dps}$ 

$$C_t = 10 \text{ dps}$$

Thus, half-life = 10 min

In next 10 min  $C_t = 5$  dps

 $\therefore$  Recorded value with error = 8 dps

14. (a)

15. (d): Arsenious sulphide is a negatively charged sol.

Hence, the coagulating powers are in the order:

$$Al^{3+} > Ba^{2+} > Na^{+}$$

**16.** (c): 
$$k = (5.0 \times 10^{11} \text{ L mol}^{-1} \text{ s}^{-1})e^{-29000/T}$$

Compare it with  $k = Ae^{-E_a/RT}$ 

$$\therefore \quad \frac{E_a}{R} = 29000$$

$$E_a = 29000 R = 29000 \times 2 \text{ cal} = 58 \text{ kcal}$$

17. (a): 
$$H_2O \longrightarrow H_2 + \frac{1}{2}O_2$$
1 mol 1 mol 0.5 mol (18 g)

$$(18 g)$$

$$W = ZIt$$

Where, Z is electrochemical equivalent.

$$Z_{\rm H_2} = \frac{\text{molar masss of H}_2}{\text{electron} \times 96500}$$

$$2 \text{ g H}_2 = \frac{2}{96500 \times 2} \times 3 \times t$$

$$t = 64333.33 \text{ s} \Rightarrow t = 17.87 \text{ h}$$

18. (b)

19. (a): 
$$2A_{(g)} \longrightarrow B_{(g)} + C_{(s)}$$
  
Initial  $P_0$  0 0

After time t  $P_0 - 2p$  p 0

After completion 0  $P_0/2$ ,  $\therefore$  Pressure after time t,  $P_t = P_0 - 2p + p = P_0 - p$ 

Total pressure after completion = 
$$P_0/2$$
  
Thus,  $P_0 - p = 300$  pascals,  $\frac{P_0}{2} = 200$  pascals

$$\therefore$$
  $P_0 = 400$  pascals,  $p = 100$  pascals

$$k = \frac{2.303}{t} \log \frac{a}{a - x} = \frac{2.303}{t} \log \frac{P_0}{P_0 - 2p}$$

$$= \frac{2.303}{10} \log \frac{400}{400 - 200} = \frac{2.303}{10} \times 0.3010 \text{ min}^{-1}$$

 $= 0.0693 \text{ min}^{-1}$ 

20. (b)



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#### One Option Correct Type

- If 0.1 M solution of  $K_4[Fe(CN)_6]$  is prepared at 300 K then its density is 1.2 g/mL. If solute is 50% dissociated, calculate  $\Delta P$  of the solution if P of pure water is 25 mm of Hg.
- (a) 0.12 (b) 0.20 (c) 10
- (d) 0.5
- Ethyl acetate  $\xrightarrow{\text{CH}_3\text{CH}_2\text{MgBr}} P$

The product *P* will be

- Which of the following is incorrect regarding the magnitude of crystal field splitting energy  $\Delta$ ?
  - (a) It depends on the coordination geometry.  $\Delta$  value for octahedral > square planar > tetrahedral.
  - (b) It depends on oxidation state of central atom  $M.\Delta$  value for  $M^{3+} > M^{2+}$ .
  - (c) It depends on whether the central atom Mbelongs to 3*d*, 4*d* or 5*d* series.
  - (d) It depends upon the nature of ligand.

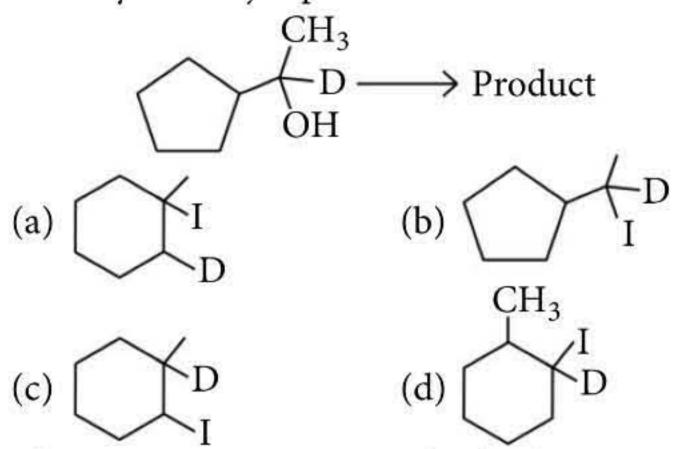
- Choose the incorrect statement pertaining to the adsorption of a gas on a solid surface.
  - (a) Adsorption is exothermic.
  - (b) Physisorption may transform into chemisorption at high temperature.
  - (c) Physisorption increases with increasing temperature but chemisorption decreases with increasing temperature.
  - (d) Chemisorption is more exothermic than physisorption, however it is usually very slow due to higher energy of activation.
- Consider the following compound (*X*):

$$HO \longrightarrow O$$
 $Br$ 
 $(X)$ 

Which of the following is correct regarding the given compound (X)?

- (i) The IUPAC name of the compound (X) is 3-bromocarbonylcyclohex-4-enoic acid.
- (ii) Trans form of compound (X) is optically inactive.
- (iii) Compound (*X*) can show optical isomerism
- (iv) Total stereoisomers of compound (*X*) is four.

- (a) i, ii and iii
- (b) ii, iii and iv
- (c) ii and iii
- (d) iii and iv
- Identify the major product:

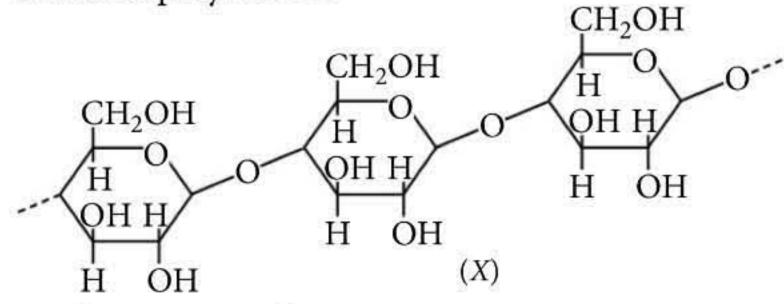


- The correct ionic reaction for leaching process is
  - (a)  $Au + 2CN^{-} \longrightarrow Au[(CN)_{2}]^{-}$
  - (b)  $Zn + 2CN^- \longrightarrow Zn[(CN)_2]^-$
  - $4Au + 8CN^{-} + 2H_2O + O_2 (air) \longrightarrow$  $4[Au(CN)_2]^-$  (soluble) +  $4OH^-$ (d)  $Zn + 4CN^{-} \longrightarrow Zn[(CN)_{4}]^{2-}$
- The total number of carboxylic acid groups in the product *P* is/are:

Calculate the emf of the cell,

Ag(s), AgIO<sub>3</sub>(s)|Ag<sup>+</sup>(xM), HIO<sub>3</sub>(1M)||Zn<sup>2+</sup>(1M)| Zn(s)  
If 
$$K_{sp} = 3 \times 10^{-8}$$
 for AgIO<sub>3</sub> and  $K_a = \frac{1}{6}$  for HIO<sub>3</sub>  
and  $E_{cell}^0$  for 2Ag + Zn<sup>2+</sup>  $\longrightarrow$  2Ag<sup>+</sup> + Zn is – 1.56 V  
(Given: log 3 = 0.48,  $\frac{2.303 \ RT}{F}$  = 0.06)

10. Which of the following is correct statement(s) about biopolymer *X* ?



- It is a non-reducing in nature.
- It exhibits mutarotation.
- It has  $\beta(C_1 C_4)$  glycosidic linkage.
- Its hydrolysis product is *D*-Galactose.
- (a) Only 1 and 2
- (b) Only 2 and 4
- - Only 1 and 3 (d) Only 1 and 4

#### More than One Options Correct Type

11. Observe the reactions I and II.  $k_1 k_1'$ ,  $k_2 k_2'$  are rate constants. Select the correct option(s).

I. 
$$\leftarrow \underbrace{\frac{(CH_3CH_2)_3N:}{[k'_1]}} CH_3 - I \xrightarrow{[k_1]} \underbrace{\frac{(CH_3CH_2)_3N:}{[k'_2]}} CH_3 - CH - CH_3 \xrightarrow{[k_2]} \underbrace{\frac{(CH_3CH_2)_3N:}{[k'_2]}} CH_3 - CH - CH_3 \xrightarrow{[k_2]} \underbrace{\frac{(CH_3CH_2)_3N:}{[k'_2]}} CH_3 - CH - CH_3 \xrightarrow{[k'_2]} \underbrace{\frac{(CH_3CH_2)_3N:}{[k'_2]}} CH_3 - CH_3$$

- (a)  $k_1 > k_1'$  (b)  $k_1 > k_2$  (c)  $k_2' > k_2$  (d)  $k_2' > k_1'$
- 12. The reaction  $A_{(g)} \longrightarrow B_{(g)} + 2C_{(g)}$  is a first order reaction with rate constant  $2.772 \times 10^{-3} \text{ sec}^{-1}$ . Reaction is started with only 0.1 mol of A in a container with volume 2 litre and is allowed to take place at constant volume and at constant temperature 300 K.  $[R = 0.082 \text{ litre atm mol}^{-1}\text{K}^{-1}]$  $\log 2 = 0.30$

Select the correct statement(s).

- (a) Concentration of C after 250 sec will be 0.05 M.
- Concentration of *C* after 250 sec will be 0.1 M.
- Partial pressure of C after 250 sec will be 2.46 atm.
- Partial pressure of C after 250 sec will be 1.23 atm.
- 13. Lead metal has a density of 11.34 g/cm<sup>3</sup> and crystallizes in a face centered lattice. Choose the correct alternatives.
  - (a) The volume of one unit cell is  $1.213 \times 10^{-22}$  cm<sup>3</sup>.
  - (b) The volume of one unit cell is  $1.214 \times 10^{-19}$  cm<sup>3</sup>.
  - (c) The atomic radius of lead is 175 pm.
  - (d) The atomic radius of lead is 155.1 pm.
- 14. Among the following statements which are correct?
  - (a) In the preparation of compounds of Xe, Bartlett had taken O<sub>2</sub>PtF<sub>6</sub> as a base compound because both O<sub>2</sub> and Xe have almost same ionisation enthalpy.
  - (b) Nitrogen does not show allotropy.
  - (c) A brown ring is formed in the ring test for  $NO_3^-$  ion. It is due to the formation of  $[Fe(H_2O)_5(NO)]^{2+}$ .
  - (d) On heating with concentrated NaOH solution in an inert atmosphere of CO<sub>2</sub>, red phosphorus gives PH<sub>3</sub> gas.
- **15.** Consider the reactions shown below:

$$CrO_4^{2-} \xrightarrow{H_2SO_4(conc.)} Cr_2O_7^{2-}$$
 $\downarrow AgNO_3(aq)$ 
 $\downarrow SO_2/H^+$ 
 $[X]$  precipitate
 $[Y]$  aqueous solution

Which of the following statement(s) are correct?

- (a) [X] is a yellow coloured precipitate.
- (b) [X] is soluble in ammonia solution.
- (c) [Y] gives green coloured solution with excess of sodium hydroxide solution.
- (d) The conversion of  $Cr_2O_7^{2-}$  to [Y] is an redox reaction.

#### SOLUTIONS

1. (a):  $K_4[Fe(CN)_6] \rightleftharpoons 4K^+ + [Fe(CN)_6]^{4-}$ Initially 1 mol 0 0
After disso.  $1 - \alpha$   $4\alpha$   $\alpha$ 

Total moles after dissociation =  $1 + 4\alpha$ As the solute is 50% dissociated therefore

$$i = 1 + (n - 1) \alpha = 1 + 4 \times \frac{1}{2} = 3$$

$$m = \frac{M \times 1000}{d \times 1000 - MM_2} = \frac{0.1 \times 1000}{1000 \times 1.2 - 0.1 \times 368}$$

$$\frac{P^0 - P_s}{P_s} = \frac{i \times m \times M_1}{1000}$$

$$= \left(\frac{3 \times 0.1 \times 1000}{1000 \times 1.2 - 0.1 \times 368}\right) \times \frac{18}{1000}$$

$$\frac{P^0}{P_s} = 1 + 4.64 \times 10^{-3}$$
;  $P_s = 24.88$  mm of Hg

 $\Delta P = 25 - 24.88 = 0.12 \text{ mm of Hg}$ 

$$C_{2}H_{5}-C-CH_{3}+C_{2}H_{5}-OMgBr$$

$$C_{2}H_{5}MgBr+C_{2}H_{5}-C=O\xrightarrow{H_{3}O^{+}}$$

$$C_{2}H_{5}-C-OH+Mg(OH)Br$$

$$C_{2}H_{5}$$

- 3. (a):  $\Delta$  for square planar > octahedral > tetrahedral.
- 4. (c)
- 5. (d):(i) The correct IUPAC name is 5-bromocarbonylcyclohex-3-enecarboxylic acid.(ii) *Trans* form of compound (X) is optically active.
- 6. (a):

- 7. (c)
- 8. (b):

$$\begin{array}{c}
 & O \\
 & O \\$$

Number of —COOH groups in product (P) is '2'.

- 9. (a):  $K_a = \frac{C\alpha^2}{1-\alpha} \Rightarrow \frac{1}{6} = \frac{\alpha^2}{1-\alpha}$  $\Rightarrow \alpha = \frac{-1 \pm \sqrt{(1)^2 + 4 \times 6 \times 1}}{12} = \frac{-1 \pm \sqrt{1 + 24}}{12} = \frac{1}{3}$   $\therefore [IO_3^-] = 1 \times \frac{1}{3} = \frac{1}{3} \Rightarrow [Ag^+] = \frac{3 \times 10^{-8}}{1/3} = 9 \times 10^{-8} \text{ M}$ Now,  $2Ag + Zn^{2+} \xrightarrow{2e^-} 2Ag^+ + Zn$   $E_{cell} = -1.56 + \frac{0.06}{2} \log \frac{1}{(9 \times 10^{-8})^2} = -1.1376 \text{ V}$
- 10. (c): Given biopolymer (X) is cellulose, which is non-reducing sugar because it lacks hemiacetal linkage. Its hydrolysis product is  $\beta$ -D-Glucose.
- 11. (a,b):  $k_1' < k_1 \Rightarrow$  due to steric hindrance of nucleophile.  $k_2' < k_2 \Rightarrow$  due to steric hindrance of nucleophile.  $k_1 > k_2 \Rightarrow$  due to steric hindrance of R X.  $k_1' > k_2' \Rightarrow$  due to steric hindrance of R X.
- 12. (a,d):  $A_{(g)} \longrightarrow B_{(g)} + 2C_{(g)}$ At time t = 0  $\frac{0.1}{2}$  0 0At time t  $\left(\frac{0.1}{2} x\right)$  x 2x

As the reaction is of first order, thus,

$$t_{1/2} = \frac{0.693}{2.772 \times 10^{-3}} = 250 \text{ s}$$

Hence, after 250 s

$$[A] = \frac{0.1}{2 \times 2} = 0.025 \,\text{M}; [C] = 2 \times \frac{0.1}{2 \times 2} = \frac{0.1}{2} \,\text{M} = 0.05 \,\text{M}$$
  
 $\Rightarrow P_c = \frac{0.1}{2} \times 0.082 \times 300 = 1.23 \,\text{atm}$ 

13. (a,c): Density = 
$$\frac{Z \times M}{N_A \times \text{volume}}$$

Volume 
$$(a^3) = \frac{4 \times 207}{6.02 \times 10^{23} \times 11.34}$$
  
 $= 1.213 \times 10^{-22} \text{ cm}^3$   
 $\therefore \text{ For } fcc, 4r = a\sqrt{2}$   
 $a = (1.213 \times 10^{-22})^{1/3}; a = 4.95 \times 10^{-8} \text{ cm}$   
 $r = \frac{4.95 \times 10^{-8} \times \sqrt{2}}{4} = 175 \text{ pm}$ 

14. (a,b,c): On heating with concentrated NaOH solution in an inert atmosphere of CO<sub>2</sub>, white phosphorus gives PH<sub>3</sub> gas.

15. (b,c,d,): 
$$Ag^{+} + CrO_{4}^{2-} \longrightarrow Ag_{2}CrO_{4} \downarrow$$

$$(X) \text{ red ppt.}$$

$$Ag_{2}CrO_{4} \downarrow + 4NH_{3} \longrightarrow 2[Ag(NH_{3})_{2}]^{+} + CrO_{4}^{2-}$$

$${}^{+4}_{3SO_{2}} + {}^{+6}_{Cr_{2}O_{7}^{2-}} + 2H^{+} \longrightarrow 2Cr^{3+} + {}^{+6}_{3SO_{4}^{2-}} + 3H_{2}O$$

$$(Y)$$

$$Cr^{3+} + 3OH^{-} \longrightarrow Cr(OH)_{3} \downarrow$$

$$(Y) \qquad (green)$$

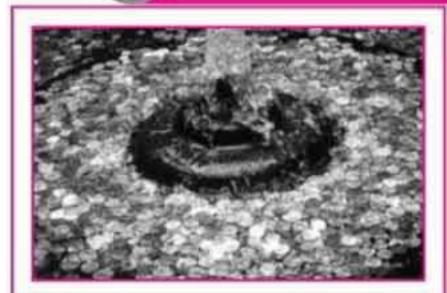
$$Cr(OH)_{3} + OH^{-} \longrightarrow [Cr(OH)_{4}]^{-}$$

$$(green coloured soluble complex)$$





### Science Behind Indian Customs



#### Throwing coins into a river

The reason given for this act is that it brings Good Luck. However, scientifically speaking, in the ancient times, most of the currency used was made of copper unlike the stainless steel coins of today. Copper is a vital metal very useful to the human body. Throwing coins in the river was one way our fore-fathers ensured we intake sufficient copper as part of the water as rivers were the only source of drinking water. Making it a custom ensured that all of us follow the practice.

#### Joining both palms together to greet

In India, people greet each other by joining their palms - termed as "Namaskar." The general reason behind this tradition is that greeting by joining both the palms means respect. However, scientifically speaking, joining both hands ensures joining the tips of all the fingers together; which are denoted to the pressure points of eyes, ears, and mind. Pressing them together is said to activate the pressure points which helps us to remember that person for a long time. And, no germs since we don't make any physical contact!





#### Why do temples have bells?

People who are visiting the temple should and will ring the bell before entering the inner sanctum where the main idol is placed. According to Agama Sastra, the bell is used to give sound for keeping evil forces away and the ring of the bell is pleasant to God. However, the scientific reason behind bells is that their ring clears our mind and helps us to stay sharp and keep our full concentration on devotional purpose.

#### Start with spice, end with sweet

Our ancestors have stressed on the fact that our meals should be started of with something spicy and sweet dishes should be taken towards the end. The significance of this eating practice is that while spicy things activate the digestive juices and acids and ensure that the digestion process goes on smoothly and efficiently, sweets or carbohydrates pulls down the digestive process. Hence, sweets were always recommended to be taken as a last item.





#### Applying Mehndi/ Henna on hands

Besides lending colour to the hands, mehndi is a very powerful medicinal herb. Weddings are stressful, and often, the stress causes headaches and fevers. As the wedding day approaches, the excitement mixed with nervous anticipation can take its toll on the bride and groom. Application of mehndi can prevent too much stress because it cools the body and keeps the nerves away from becoming tense.



Chapterwise practice questions for CBSE Exams as per the latest pattern and marking scheme issued by CBSE for the academic session 2019-20.

Series 3

General Principles and Processes of Isolation of Elements/ The p-Block Elements (Group 15 to 18)

Time Allowed: 3 hours Maximum Marks: 70

#### **GENERAL INSTRUCTIONS**

- All questions are compulsory.
- (ii) Section A: Q. no. 1 to 20 are very short answer-objective questions and carry 1 mark each.
- (iii) Section B: Q. no. 21 to 27 are short answer questions and carry 2 marks each.
- (iv) Section C: Q. no. 28 to 34 are long answer-I questions and carry 3 marks each.
- (v) Section D: Q. no. 35 to 37 are long answer-II questions and carry 5 marks each.
- (vi) There is no overall choice in the question paper. However, internal choices are given in the sections.
- (vii) Use log tables if necessary, use of calculator is not allowed.

#### **SECTION-A**

- Of the following, the metal that cannot be obtained by the electrolysis of aqueous solution of their salts is
  - (a) Ag
- (b) Mg
- (c) Cu
- (d) Cr
- Hydrolysis of one mole of peroxodisulphuric acid produces
  - (a) two moles of sulphuric acid
  - (b) two moles of peroxomonosulphuric acid
  - (c) one mole of sulphuric acid and one mole of peroxomonosulphuric acid
  - (d) one mole of sulphuric acid, one mole of peroxomonosulphuric acid and one mole of hydrogen peroxide.
- Among the following statements the incorrect one
  - (a) calamine and siderite are carbonates
  - (b) argentite and cuprite are oxides
  - (c) zinc blende and iron pyrites are sulphides
  - (d) malachite and azurite are ores of copper.

- For which ore of the metal, froth floatation method is used for concentration?
  - (a) Horn silver
- (b) Bauxite
- (c) Cinnabar
- (d) Haematite
- 5. Which one of the following oxides of nitrogen is blue solid?
  - (a) NO
- (b)  $N_2O_3$  (c)  $N_2O$
- (d)  $N_2O_5$
- 6. Which of the following is incorrect?
  - (a)  $O_2$  is weaker oxidant than  $O_3$ .
  - (b)  $O_3$  has larger bond length than  $O_2$ .
  - (c) Both  $O_2$  and  $O_3$  are paramagnetic.
  - (d)  $O_2$  is linear and  $O_3$  is angular in shape.
- 7. Copper is extracted from copper pyrites ore by heating in a blast furnace. The method is based on the principle that
  - (a) copper has more affinity for oxygen than sulphur at high temperature
  - (b) iron has less affinity for oxygen than sulphur at high temperature

- (c) sulphur has less affinity for oxygen at high temperature
- (d) copper has less affinity for oxygen than sulphur at high temperature.
- 8. During smelting an additional substance is added which combines with impurities to form a fusible product. It is known as
  - (a) slag
- (b) mud
- (c) gangue (d) flux.
- 9. Which one of following statements about halogens is correct?
  - (a) F<sub>2</sub> has lower bond dissociation energy than Cl<sub>2</sub>.
  - (b) van der Waals' forces are the weakest in iodine.
  - (c) HF is the strongest hydrohalic acid.
  - (d) All halogens show variable oxidation states.
- 10. Which of the following statements about noble gases is false?
  - (a) They are used to provide inert atmosphere in many chemical reactions.
  - (b) They are only sparingly soluble in water.
  - (c) They form diatomic molecules.
  - (d) Some of them are used in discharge tubes and signs which are used for advertising purposes.
- 11. In nature, metal *A* is found in free state, while metal *B* is found in the form of its compounds. Which of these two will be nearer to the top of the activity series of metals?
- 12. Why is limestone added to the ore in the extraction of iron in blast furnace?
- 13. Why does NH<sub>3</sub> act as a Lewis base?
- **14.** In the extraction of Al, impure Al<sub>2</sub>O<sub>3</sub> is dissolved in conc. NaOH to form sodium aluminate and leaving impurities behind. What is the name of this process?
- 15. Why does the reactivity of nitrogen differ from phosphorus?
- 16. Why has it been difficult to study the chemistry of radon?
- 17. Although thermodynamically feasible, in practice, magnesium metal is not used for reduction of alumina in the metallurgy of aluminium. Why?
- 18. What is the role of cryolite in the extraction of aluminium?

(2018C, AI 2016, 2015 C, Delhi, AI 2013, Delhi 2012, AI 2010)

- 19. Account for the following:
  Sulphur in vapour form exhibits paramagnetic behaviour. (Delhi 2019, AI 2014 Foreign 2014, 2011, Delhi 2012, 2011C)
- 20. PCl<sub>5</sub> acts as an oxidising agent. Why?

#### **SECTION-B**

- 21. How is 'cast iron' different from 'pig iron'?
- 22. Give disproportionate reaction of H<sub>3</sub>PO<sub>3</sub>.

#### OR

Starting from elemental sulphur, how would you prepare (i) S<sub>2</sub>Cl<sub>2</sub> and (ii) SF<sub>6</sub>?

- 23. The choice of a reducing agent in a particular case depends on thermodynamic factors. How far do you agree with this statement? Support your opinion with examples.
- 24. Why does chlorine water lose its yellow colour on standing?
- 25. Name the metals which are associated with the following terms in their extractions from ores :
  - (i) Bessemer's converter (ii) Blast furnace
  - (iii) Alumino-thermic process
  - (iv) Magnetic separation

#### OR

The reaction,

 $Cr_2O_3 + 2Al \longrightarrow Al_2O_3 + 2Cr$ ;  $\Delta_rG^\circ = -421$  kJ is thermodynamically feasible as is apparent from the Gibbs free energy value. Why does the reaction not take place at room temperature?

- **26.** Account for the following:
  - (i) The boiling points of noble gases increase with the increase in atomic number.
  - (ii) Neon is generally used in warning signal illumination.
- 27. Sulphur dioxide is a powerful reducing agent in an alkaline medium than in acidic medium. Explain.

#### SECTION-C

- 28. Write the chemical reactions involved in the process of extraction of Gold. Explain the role of dilute NaCN and Zn in this process.
- 29. Give an example of a reaction in which H<sub>2</sub>SO<sub>4</sub> behaves as
  - (i) a strong acid
  - (ii) a dehydrating agent
  - (iii) an oxidising agent.

#### 30. Explain:

- (i) NF<sub>3</sub> is an exothermic compound whereas NCl<sub>3</sub> is an endothermic compound.
- (ii)  $I_3^-$  ion exists but  $F_3^-$  does not.

#### OR

Answer the following:

- (i) Iodine is liberated when KI is added to a solution containing Cu<sup>2+</sup> ions but Cl<sub>2</sub> is not liberated when KCl is added to a solution of Cu<sup>2+</sup> ions.
- (ii) Sodium thiosulphate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>) reacts with Cl<sub>2</sub> and I<sub>2</sub> to give different oxidation products. Give the chemical equation and plausible explanations.
- 31. (i) What do you mean by smelting?
  - (ii) Distinguish between calcination and roasting.
- 32. Give reason:
  - (i) Metals like Cu, Ag, Zn, Hg and Pb occur in nature as sulphides rather than oxides.
  - (ii) Graphite is used as an electrode but not diamond.
  - (iii) Copper obtained in the extraction from copper pyrites have a blistered appearance.
- 33. Describe the Contact process for the manufacture of sulphuric acid with special reference to the reaction conditions, catalysts used and yield in the process. (No diagram is required.)

#### (Delhi 2015C, 2012C)

- **34.** (i) Explain, why a basic flux is used in the extraction of iron but an acidic flux is used in case of copper?
  - (ii) For the extraction of iron in a blast furnace what is used as a reducing agent?
  - (iii)In which part of the blast furnace the temperature is maximum?

#### OR

Give briefly the isolation of magnesium from seawater by the Dow's process. Give equations for the steps involved.

#### SECTION-D

35. A translucent white waxy solid *A* on heating in an inert atmosphere is converted into its allotropic form *B*. Allotrope *A* on reaction with very dilute aqueous KOH liberates a highly poisonous gas *C* having rotten fish smell. With excess of chlorine,

C forms D which hydrolyses to a compound E. Identify A to E.

#### OR

- (a) Account for the following:
  - (i) NH<sub>3</sub> has higher boiling point than PH<sub>3</sub>.
  - (ii) H<sub>3</sub>PO<sub>3</sub> is diprotic acid.
  - (iii) OF<sub>2</sub> should be called oxygen difluoride and not fluorine oxide.
- (b) Complete and balance the following chemical equations:
  - (i)  $P_4O_{10} + PCl_5 \longrightarrow$
  - (ii)  $SnCl_4 + C_2H_5Cl + Na \longrightarrow$
- 36. Write short notes on
  - (i) Goldschmidt thermite process
  - (ii) Self-reduction
  - (iii) Electrolytic reduction

#### OR

- (a) Describe the principle involved in each of the following processes.
  - (i) Mond process for refining of nickel.
  - (ii) Column chromatography for purification of rare elements.
- (b) Write down the reactions which occur in upper, middle and lower zones in the blast furnace during the extraction of iron from iron ore.
- **37.** How would you prepare :
  - (i) Cl<sub>2</sub> gas in the laboratory
  - (ii) HF from CaF<sub>2</sub>
- (iii) Br, from sea water
- (iv) I<sub>2</sub> from NaIO<sub>3</sub>
- (v) HBr from NaBr

#### OR

- (a) Arrange the following in:
  - (i) HCl, HBr, HF, HI ⇒ increasing bond strength
  - (ii) HOCl, HOClO<sub>2</sub>, HOClO<sub>3</sub>, HOClO ⇒ increasing order of thermal stability.
  - (iii)  $CO_2$ ,  $N_2O_5$ ,  $SiO_2$ ,  $SO_3 \Rightarrow$  increasing order of acidic character
- (b) Xenon has closed shell configuration but is known to give compounds with fluorine.

#### SOLUTIONS

- 1. (b)
- 2. (c) :  $H_2S_2O_8 + H_2O \rightarrow H_2SO_4 + H_2SO_5$ peroxodisulphuric sulphuric acid peroxomonoacid sulphuric acid
- 3. (b) : Argentite (Ag<sub>2</sub>S) is a sulphide ore.

- 4. (c): Froth floatation method is used for concentration of sulphide ores like cinnabar (HgS).
- 5. (b):  $N_2O_3$  exists as blue solid at a very low temperature.
- 6. (c): O<sub>3</sub> is not paramagnetic, it is diamagnetic.
- 7. (a)
- 8. (d): Flux is added during smelting which combines with impurities to form a fusible product.
- 9. (a): F<sub>2</sub> has lower bond dissociation energy than Cl<sub>2</sub> due to strong inter-electronic repulsions.
- 10. (c): Noble gases exist as monoatomic molecules.
- 11. The metal *B* will be nearer to the top of the activity series because it is a reactive metal.
- 12. To remove impurity of silica as fusible slag.
- 13. Nitrogen atom in NH<sub>3</sub> has one lone pair of electrons which is available for donation where there is a need of electrons. Therefore, ammonia acts as a Lewis base.
- 14. Leaching
- 15. The reactivity of nitrogen differs from that of phosphorus due to the absence of d-orbitals in its valence shell.
- 16. Because radon is radioactive and keeps disintegrating continuously and changes into newer element.
- 17. Below the temperature (1623 K) corresponding to the point of intersection of Al<sub>2</sub>O<sub>3</sub> and MgO curves in Ellingham diagram magnesium can reduce alumina. But magnesium is a much costlier metal than aluminium and hence the process will be uneconomical.
- **18.** Purified alumina (Al<sub>2</sub>O<sub>3</sub>) is mixed with cryolite (Na<sub>3</sub>AlF<sub>6</sub>) which lowers the melting temperature of electrolyte and also increases its conductivity.
- 19. At elevated temperature, sulphur vapour exists as  $S_2$  molecule which has two unpaired electrons in the antibonding  $\pi^*$ -orbitals like  $O_2$  hence, exhibits paramagnetism.
- **20.** The oxidation state of phosphorus in  $PCl_5$  is +5. As P has five electrons in its valence shell, it cannot increase its oxidation state beyond +5 by donating electrons. It can decrease its oxidation number from +5 to +3 or some lower value. So,  $PCl_5$  acts as an oxidising agent.
- 21. The iron obtained from the blast furnace is called pig iron. Pig iron contains about 4% carbon and many impurities such as S, P, Si, Mn etc. Cast iron is made

by melting pig iron with scrap iron and coke using hot air blast. Cast iron contains about 3% carbon and is extremely hard and brittle.

22. On heating, H<sub>3</sub>PO<sub>3</sub> forms H<sub>3</sub>PO<sub>4</sub> and PH<sub>3</sub>.

$$4H_3PO_3 \xrightarrow{\Delta} PH_3 + 3H_3PO_4$$

Thus, H<sub>3</sub>PO<sub>3</sub> undergoes disproportionation to form PH<sub>3</sub> in which it is reduced and H<sub>3</sub>PO<sub>4</sub> in which it is oxidised.

#### OR

- (i) By passing chlorine gas through boiling sulphur :  $S_{8(l)} + 4Cl_{2(g)} \longrightarrow 4S_2Cl_{2(l)}$ Orange-yellow
- (ii)  $S_8 + 24F_{2(g)} \longrightarrow 8SF_{6(g)}$ Vapours
- **23.** The direction of any reaction/process at any temperature and pressure depends upon the change in the Gibbs' free energy ( $\Delta G$ ) during the process. For a favourable process,  $\Delta G$  should be negative, *i.e.*, the free energy of the system must decrease.

During the reduction of haematite to iron, carbon is used. At temperature below 983 K, haematite is reduced by CO, whereas at higher temperature carbon is a better reducing agent.

**24.** Chlorine is moderately soluble in water, forming a pale-yellow solution. It is usually called chlorine water. The pale-yellow colour is due to formation of hypochlorous acid (HOCl).

$$Cl_2 + H_2O \longrightarrow HCl + HClO$$

As HClO is unstable, the pale-yellow colour disappears on standing.

$$HClO \longrightarrow HCl + [O]$$

- 25. (i) Bessemer's converter Copper, Iron
- (ii) Blast furnace Iron
- (iii) Alumino-thermic process Iron, Chromium
- (iv) Magnetic separation Tin, Chromium, Manganese

#### OR

As Gibbs free energy for the above reaction is negative, the reaction is feasible. But thermodynamics does not tell us the conditions under which the reaction will be spontaneous. The temperature for the reaction to be spontaneous may be higher than the room temperature. Usually, activation is essential even for thermodynamically feasible reactions, therefore, heating is required.

26. (i) With the increase in the molecular mass, the size of the noble gas is increased consequently the extent of van der Waals' force is also increased among

the molecules. Due to the increase in the forces with the increase in molar mass, the boiling point will also increase.

- (ii) Because neon light is visible through mist and fog and that too from long distances.
- 27. Sulphur dioxide acts as reducing agent in an alkaline medium as follows:

$$SO_2 + 2OH^-_{(aq)} \Longrightarrow SO_4^{2-}_{(aq)} + 2H^+_{(aq)} + 2e^-$$

The reaction proceeds in the forward direction with increase in the concentration of OH<sup>-</sup> ions. Thus SO<sub>2</sub> can act as a powerful reducing agent in alkaline medium. In an acidic medium, greater concentration of H<sup>+</sup> ions shifts the equilibrium in the backward direction, thus making sulphur dioxide a weaker reducing agent.

28. 
$$4\text{Au}_{(s)} + 8\text{CN}_{(aq)}^{-} + 2\text{H}_{2}\text{O}_{(l)} + \text{O}_{2(g)} \rightarrow 4[\text{Au}(\text{CN})_{2}]_{(aq)}^{-} + 4\text{OH}_{(aq)}^{-}$$

 $2[Au(CN)_2]_{(aq)}^- + Zn_{(s)} \rightarrow [Zn(CN)_4]_{(aq)}^{2-} + 2Au_{(s)}$ NaCN is used for leaching of gold ore in the presence of air to form soluble gold complex from which metal is displaced by adding more reactive metal. Role of zinc is to recover gold from the complex by displacement reaction.

29. (i) 
$$Na_2CO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + CO_2 + H_2O_3$$

(ii) 
$$C_{12}H_{22}O_{11} + H_2SO_4(conc.) \rightarrow 12C + 11H_2O$$
  
Sugar

(iii) 
$$H_2SO_4 \longrightarrow H_2O + SO_2 + O] \times 2$$
  
 $C + 2O \longrightarrow CO_2$   
 $2H_2SO_4 + C \longrightarrow 2SO_2 + CO_2 + 2H_2O$ 

**30.** (i) Bond dissociation energy of  $F_2$  (158.8 kJ mol<sup>-1</sup>) is much lower than that of  $Cl_2$  (242.6 kJ mol<sup>-1</sup>). Therefore, energy released during the formation of NF<sub>3</sub> molecule is more than the energy needed to break N<sub>2</sub> (941.4 kJ mol<sup>-1</sup>) and F<sub>2</sub> molecules into individual atoms. In other words, formation of NF<sub>3</sub> is an exothermic process, *i.e.*, NF<sub>3</sub> is an exothermic compound.

$$N_{2(g)} + 3F_{2(g)} \longrightarrow 2NF_{3(g)}; \quad \Delta H = -244.2 \text{ kJ mol}^{-1}$$
  
 $N_{2(g)} + 3Cl_{2(g)} \longrightarrow 2NCl_{3(g)}; \quad \Delta H + 512.2 \text{ kJ mol}^{-1}$ 

(ii) If  $F_3^-$  is formed, then central F-atom would have 10 electrons in its valence shell. But that is not possible because F cannot extend its octet due to the absence of d-orbitals. Hence,  $F_3^-$  does not exist.

#### OR

(i) I<sup>-</sup> ions are strong reducing agents and, therefore, they reduce Cu<sup>2+</sup> to Cu<sup>+</sup> ions and themselves get oxidised to I<sub>2</sub>.

$$2I^- + Cu^{2+} \longrightarrow CuI_2$$
(Unstable)

$$2CuI_2 \longrightarrow Cu_2I_2 + I_2$$

While Cl<sup>-</sup> acts as reductant only in presence of strong oxidant.

(ii)  $Cl_2$  is a stronger oxidising agent than  $I_2$  and, therefore, it oxidises  $Na_2S_2O_3$  to  $NaHSO_4$ . In this reaction, oxidation number of sulphur increases from +2 to +6.

$$Na_2^{+2}S_2O_3 + 4Cl_2 + 5H_2O \longrightarrow 2NaHSO_4 + 8HCl$$

With iodine, tetrathionate is obtained in which oxidation number of sulphur increases from 2 to 2.5.

$$2\text{Na}_2^{+2}\text{S}_2^{+2}\text{O}_3 + \text{I}_2 \longrightarrow 2\text{NaI} + \text{Na}_2^{+2.5}\text{Sodium tetrathionate}$$

31. (i) The reduction of an ore into molten metal at a high temperature, using reducing agents like H<sub>2</sub>, coke, CO gas, aluminium, magnesium metal, etc. is known as smelting. This chemical reduction is generally carried out in blast furnace.

(ii)

	Calcination	Roasting
(i)	heating the ore in limited supply or	It is the process in which the ore is heated in a free supply of air below its fusion temperature.
(ii)	remove moisture, and	This process helps to remove moisture, volatile impurities as oxides and to convert ferrous to ferric state.
(iii)	hydroxide ores and carbonate ores are	Sulphide ores are generally converted to oxide form in this process. $e.g.$ , $2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2^{\uparrow}$ $Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2^{\uparrow}$

**32.** (i) The cation of the metals, *i.e.*,  $Cu^{2+}$ ,  $Zn^{2+}$ ,  $Ag^+$  and  $Hg^{2+}$  have pseudo inert gas configuration, (n-1)  $s^2$   $p^6$   $d^{10}$  and  $Pb^{2+}$  has the configuration (n-1)  $d^{10}$   $ns^2$   $np^6$  (inert pair effect). Due to these

configurations, they have high polarising power. As a result of this, they can easily polarise bigger sulphide ion than the smaller oxide ion. Hence, the sulphides of these metals are more stable and these metals occur in nature as their sulphides rather than oxides.

(ii) Graphite is a good conductor of electricity due to the presence of free electrons within its layers. Diamond, on the other hand, is not a good conductor of electricity since no free electrons are present in its structure. Therefore, it cannot be used as an electrode. (iii) Copper obtained in the extraction from copper parities has a blistered appearance due to the evolution

pyrites has a blistered appearance due to the evolution of SO<sub>2</sub>.

$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$$
  
 $2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2$ 

33. Contact process: It involves following steps:

(i) Burning of sulphur or sulphide ore in air to generate SO<sub>2</sub>.

$$S + O_2 \longrightarrow SO_2$$
  
 $4FeS_2 + 11O_2 \longrightarrow 8SO_2 + 2Fe_2O_3$ 

(ii) Conversion of  $SO_2$  to  $SO_3$  by reaction with oxygen in the presence of  $V_2O_5$  catalyst.

$$2SO_{2(g)} + O_{2(g)} \xrightarrow{V_2O_5} 2SO_{3(g)};$$

$$\Delta_r H^\circ = -196 \text{ kJ mol}^{-1}$$

(iii) The  $SO_3$  gas from the catalytic converter is absorbed in conc.  $H_2SO_4$  to form oleum  $(H_2S_2O_7)$ . Dilution of oleum with water gives  $H_2SO_4$  of desired concentration.

$$SO_3 + H_2SO_4 \longrightarrow H_2S_2O_7$$
 (oleum)  
 $H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$ 

**34.** (i) Iron ore contains silica as the impurity, so for extraction of iron from its ore a basic flux (limestone) is required.

$$\begin{array}{ccc} {\rm CaCO_3} & \longrightarrow {\rm CaO} + {\rm CO_2} \\ {\rm SiO_2} & + & {\rm CaO} & \longrightarrow & {\rm CaSiO_3} \\ {\rm Acidic-} & {\rm Basic-} & {\rm Slag} \\ {\rm impurity} & {\rm flux} \end{array}$$

On the other hand copper ore contains ferrous sulphide as the impurity. After roasting the ore ferrous sulphide is converted to ferrous oxide, which is basic in nature. Therefore acidic flux (SiO<sub>2</sub>) is required for extraction of copper.

(ii) For the extraction of iron, coke or charcoal is used as reducing agent. But the actual reducing agent is carbon monoxide, formed from coke.

(iii) At the hearth (near the bottom) of the furnace, the temperature is maximum (1600°C).

#### OR

In sea water MgCl<sub>2</sub> is also present which can be precipitated as Mg(OH)<sub>2</sub> by means of addition of lime water.

$$MgCl_2 + Ca(OH)_2 \longrightarrow Mg(OH)_2 \downarrow + CaCl_2$$
  
 $Mg(OH)_2 \xrightarrow{\Delta} MgO + H_2O$   
 $MgO + C + Cl_2 \xrightarrow{\Delta} MgCl_2 + CO\uparrow$ 

This MgCl<sub>2</sub> in fused state is mixed with fused KCl and then this fused mixture is electrolysed in Fe crucible, which acts as cathode and graphite rod is used as anode. The electrodes are separated by a porous diaphragm and electrolysis is carried out in an atmosphere of coal gas (inert atmosphere).

$$MgCl_2 \longrightarrow Mg^{2+} + 2Cl^-$$
  
At anode:  $2Cl^- \longrightarrow Cl_2 + 2e^-$   
At cathode:  $Mg^{2+} + 2e^- \longrightarrow Mg$ 

**35.** (i) As the translucent white waxy solid A on heating in an inert atmosphere, is converted into its allotrope B, therefore, solid A is white phosphorus.

White 
$$P \xrightarrow{\text{Heat, inert gas}} \text{Red } P$$
(A) (B)

(ii) As *A* on heating with dilute solution of KOH gives a highly poisonous gas *C* having the smell of rotten fish, it confirms that *A* is white phosphorus and *C* is phosphine (PH<sub>3</sub>).



What did the thermometer say to the graduated cylinder?

YOU MAY HAVE

GRADUATED

MANY DEGRES

$$P_{4(s)}$$
 +  $3KOH_{(aq)}$  +  $3H_2O_{(l)} \xrightarrow{Heat}$ 

White phosphorus (A)

 $3KH_2PO_2$  +  $PH_{3(g)} \uparrow$ 

Phosphine (C)

(iii) Phosphine C reacts with excess of  $Cl_2$  to form a compound D which on hydrolysis gives compound E, therefore, D is  $PCl_5$ .

$$\begin{array}{ccccc} \mathrm{PH}_3 & + & 4\mathrm{Cl}_2 & \longrightarrow & \mathrm{PCl}_5 & + & 3\mathrm{HCl} \\ (\mathit{C}) & & & \mathrm{Phosphorus} \\ & & & & \mathrm{pentachloride} \, (\mathit{D}) \end{array}$$

$$\begin{array}{ccc} \mathrm{PCl}_5 + 4\mathrm{H}_2\mathrm{O} & \longrightarrow & \mathrm{H}_3\mathrm{PO}_4 & + & 5\mathrm{HCl} \\ (D) & \mathrm{Phosphoric\ acid\ }(E) & \end{array}$$

Thus, A is white phosphorus, B is red phosphorus, C is phosphine, D is  $PCl_5$  and E is phosphoric acid.

OR

- (a) (i) N is more electronegative and smaller in size than P, hence NH<sub>3</sub> molecules have intermolecular H-bonds, therefore its boiling point is exceptionally high. In PH<sub>3</sub> only weak van der Waals' forces are present and no hydrogen bond is there. Due to this reason NH<sub>3</sub> has higher boiling point than PH<sub>3</sub>.
- (ii) In H<sub>3</sub>PO<sub>3</sub> two hydrogen are attached to the oxygen (ionisable) and one hydrogen is attached to phosphorus (non-ionisable). HOH OH Due to this reason only two hydrogens can be released as H<sup>+</sup> hence it is diprotic.
- (iii) Fluorine is more electronegative than oxygen hence OF<sub>2</sub> should be called oxygen difluoride (because the name of less electronegative element comes first and then the name of more electronegative atom).

(b) (i) 
$$P_4O_{10} + 6PCl_5 \longrightarrow 10POCl_3$$

(ii) 
$$\operatorname{SnCl}_4^4 + 2\operatorname{C}_2\operatorname{H}_5\operatorname{Cl} + 2\operatorname{Na} \longrightarrow \operatorname{Na}_2\operatorname{SnCl}_6 + \operatorname{C}_4\operatorname{H}_{10}$$

**36. (i)** Goldschmidt thermite process: Certain oxides are not satisfactorily reduced by carbon. In such cases, aluminium is used as a reducing agent. A mixture of metallic oxide and aluminium powder is ignited in a closed crucible by means of lighted magnesium ribbon. Metals like chromium, manganese etc. are extracted by thermite process as illustrated below.

$$Cr_2O_3 + 2Al \longrightarrow Al_2O_3 + 2Cr$$
  
 $3Mn_3O_4 + 8Al \longrightarrow 4Al_2O_3 + 9Mn$ 

The reaction is highly exothermic and the heat produced is sufficient to melt the metal.

(ii) Self-reduction process: In some cases no extra reducing agent is required. A part of the sulphide ore is changed to oxide or sulphate which then reacts with the remaining part to give the metal and sulphur dioxide. Copper and lead are obtained by this method.

$$2Cu_{2}S + 3O_{2} \longrightarrow 2Cu_{2}O + 2SO_{2}$$

$$Cu_{2}S + 2Cu_{2}O \longrightarrow 6Cu + SO_{2}$$

$$2PbS + 3O_{2} \longrightarrow 2PbO + 2SO_{2}$$

$$PbS + 2O_{2} \longrightarrow PbSO_{4}$$

$$PbSO_{4} + PbS \longrightarrow 2Pb + 2SO_{2}$$

(iii) Electrolytic reduction: The carbon reduction methods are not applicable for the highly electropositive and chemically active metals such as alkali metals, alkaline earth metals, aluminium etc. The oxides of these metals are very stable and have to be heated very strongly with carbon in order to reduce them to metals. But at high temperature, these metals combine with carbon to form carbides, thus creating problem. Hence these metals are extracted by the electrolytic reduction of their fused halides. The metal is liberated at the cathode. Aluminium is however obtained by the electrolytic reduction of alumina (Al<sub>2</sub>O<sub>3</sub>) dissolved in molten cryolite (Na<sub>3</sub>AlF<sub>6</sub>).

#### OR

(a) (i) Mond's process: Impure nickel is treated with carbon monoxide at 60-80°C to form volatile nickel carbonyl which decomposes to give pure nickel at 180°C.

Ni + 4CO 
$$\xrightarrow{60 - 80^{\circ}\text{C}}$$
 Ni(CO)<sub>4</sub>  $\xrightarrow{180^{\circ}\text{C}}$  Ni + 4CO

Impure

Pure

- (ii) Column chromatography is the simplest method. This is based on adsorption phenomenon. The extent of adsorption of various constituents present in the mixture liquid (moving phase) varies with a given adsorbent (stationary phase). The common adsorbents used are alumina, silica gel, magnesium oxides etc.
- (b) Following reactions occur in the blast furnace:
- (i) Lower zone of the blast furnace:

$$C + O_2 \longrightarrow CO_2 + heat$$
  
 $C + CO_2 \longrightarrow 2CO$ 

Coke is burnt to give CO<sub>2</sub>, which then rises upwards and reduced to carbon monoxide. Temperature is upto 2200 K at lower part of the blast furnace.

(ii) Middle zone of the blast furnace: CO and heat move up in the furnace. The temperature range in the middle zone of the blast furnace is 900-1500 K.

$$FeO + CO \longrightarrow Fe + CO_2$$

Limestone is also decomposed to CaO which removes silicate impurity of the ore as slag.

$$\begin{array}{c} \text{CaCO}_{3} \xrightarrow{1100 \text{ K}} \text{CaO} + \text{CO}_{2} \\ \text{C} + \text{CO}_{2} \longrightarrow 2\text{CO} \\ \text{CaO} + \text{SiO}_{2} \longrightarrow \text{CaSiO}_{3} \\ \text{Slag} \end{array}$$

(iii) Upper zone of the blast furnace: Temperature range in this zone is 500-800 K.

$$3\text{Fe}_2\text{O}_3 + \text{CO} \longrightarrow 2\text{Fe}_3\text{O}_4 + \text{CO}_2$$
  
 $\text{Fe}_2\text{O}_3 + \text{CO} \longrightarrow 2\text{FeO} + \text{CO}_2$   
 $\text{Fe}_3\text{O}_4 + 4\text{CO} \longrightarrow 3\text{Fe} + 4\text{CO}_2$ 

Impure iron obtained from blast furnace is known as pig iron and cast into pigs (blocks).

**37.** (i) When HCl is oxidesed by MnO<sub>2</sub> or KMnO<sub>4</sub>, Cl<sub>2</sub> is obtained.

$$\begin{split} \operatorname{MnO}_{2(s)} + 4\operatorname{HCl}_{(aq)} &\longrightarrow \operatorname{MnCl}_{2(aq)} + \operatorname{Cl}_{2(g)} + 2\operatorname{H}_2\operatorname{O}_{(l)} \\ 2\operatorname{KMnO}_{4(s)} + 16\operatorname{HCl}_{(aq)} &\longrightarrow 2\operatorname{MnCl}_{2(aq)} + 2\operatorname{KCl}_{(aq)} \\ &\quad + 5\operatorname{Cl}_{2(g)} + 8\operatorname{H}_2\operatorname{O}_{(l)} \end{split}$$

(ii) When calcium fluoride (fluorospar) is treated with conc. H<sub>2</sub>SO<sub>4</sub>. HF is obtained.

$$CaF_{2(s)} + H_2SO_{4(aq)} \longrightarrow CaSO_{4(s)} + 2HF_{(g)}$$

(iii) Sea water is the most important source of commercial bromine.

The sea water is slightly acidified and then treated with chlorine to liberate bromine.

$$2Br^- + Cl_2 \longrightarrow 2Cl^- + Br_2$$

(iv) When chile saltpetre which contains sodium iodate (NaIO<sub>3</sub>) is dissolved in hot water and allowed to cool it crystallizes and can be separated from residue (richer with iodate ion) left in mother liquor. The mother liquor is treated with a calculated amount of sodium hydrogen sulphite solution to precipitate out iodine.

$$2\text{NaIO}_3 + 5\text{NaHSO}_3 \longrightarrow 3\text{NaHSO}_4 + 2\text{Na}_2\text{SO}_4 + \text{H}_2\text{O} + \text{I}_2$$

(v) When NaBr is treated with non-oxidising acid like H<sub>3</sub>PO<sub>4</sub>, HBr is obtained.

$$3\text{NaBr} + \text{H}_3\text{PO}_4 \longrightarrow 3\text{HBr} + \text{Na}_3\text{PO}_4$$

OR

The strength of H—X bond decreases as we move down the group. On moving down the group the atomic size increases so H—X bond length increases. The larger the H—X bond length, lower is the bond energy and so lesser is the bond strength.

As the oxidation state of Cl increases (or the number of oxygen atoms increases), the –ve charge dispersal becomes more and more from Cl atom due to higher electronegativity value of oxygen. Lesser the charge on Cl atom more is the stability.

(iii) 
$$SiO_2 < CO_2 < N_2O_5 < SO_3$$

In case of oxides of non-metals, the acid strength

increases with increase in oxidation state. The oxidation states of various elements are Si = +4, C = +4, N = +5, S = +6 in the given oxides. Due to the small size of C-atom,  $CO_2$  is more acidic than  $SiO_2$ .

(b) Xenon atom has large size and lower ionisation potential in comparison to He, Ne, Ar and Kr. The outermost energy shell has *d*-orbitals. The paired electrons of valence shell can be unpaired and the electrons are shifted to *d*-orbitals under suitable conditions. The unpaired electrons are shared by fluorine atoms and covalent bonds are formed. In this way, xenon forms compounds with fluorine.





## How to produce natural gas while storing carbon dioxide!!!

New research shows that injecting air and carbon dioxide into methane ice deposits buried beneath the Gulf of Mexico could unlock vast natural gas energy resources while helping fight climate change by trapping the carbon dioxide underground.

The study used computer models to simulate what happens when mixtures of carbon dioxide and air are injected into deposits of methane hydrate, an ice-like, water-rich chemical compound that forms naturally in high-pressure, low-temperature environments, such as deep in the Gulf of Mexico and under Arctic permafrost.

This research is the next step in solving two significant global challenges: energy security and carbon storage.

In the process, the nitrogen in the injected air sweeps the methane toward a production well and allows carbon dioxide to take its place, researchers said. The beauty of this approach is that it extracts natural gas from methane hydrate deposits and at the same time stores carbon dioxide, a greenhouse gas, in a deep environment where it is unlikely to be released into the atmosphere where it could contribute to climate change.

The next step is to test their findings in a lab. The scientists are currently testing the method in a specialized facility that can store and test methane hydrate.

"Two things are really cool. First, we can produce natural gas to generate energy and sequester CO<sub>2</sub>," said the scientist. "Second, by swapping the methane hydrate with CO<sub>2</sub> hydrate, we disturb the (geologic) formation less, lowering the environmental impact, and we make the process energetically more efficient."

# MONTHLY TEST DRIVE MONTHLY TEST MONTHLY TE

This specially designed column enables students to self analyse their extent of understanding of specified chapters. Give yourself four marks for correct answer and deduct one mark for wrong answer. Self check table given at the end will help you to check your readiness.

Total Marks: 120 Haloalkanes and Haloarenes / Alcohols, Phenols and Ethers

#### Time Taken: 60 Min.

#### **NEET / AIIMS**

#### Only One Option Correct Type

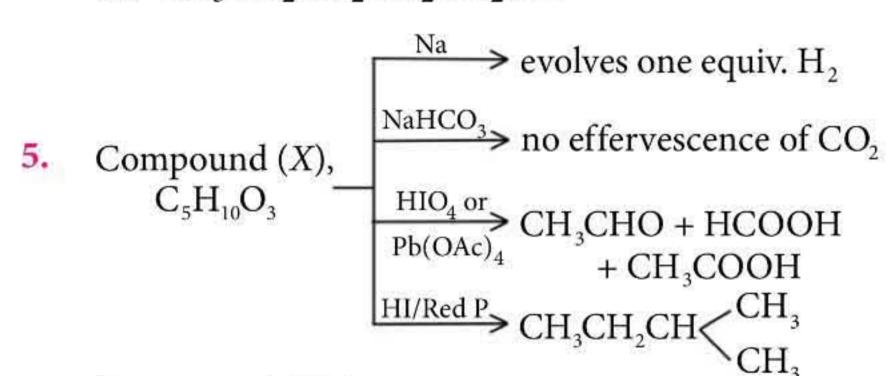
- 1. Which of the following compounds on reaction with CH<sub>3</sub>MgBr will give a tertiary alcohol?
  - (a)  $C_2H_5CHO$
- (b) C<sub>2</sub>H<sub>5</sub>COOCH<sub>3</sub>
- (c) C<sub>2</sub>H<sub>5</sub>COOH
- (d) O
- 2. The decreasing order of rate of S<sub>N</sub>2 reaction is

I 
$$CH_3 - Cl$$

II 
$$CH_3 - C - CH_2 - CI$$

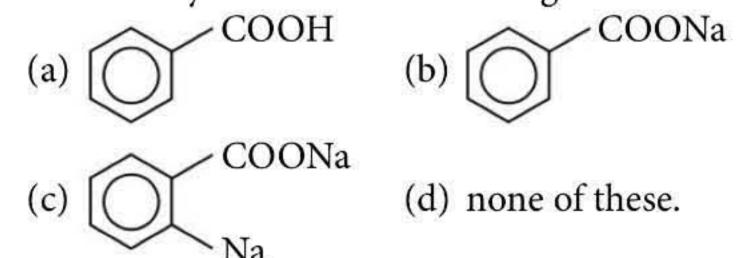
IV 
$$CH_3 - CH_2 - Cl$$

- (a) IV > III > II > I
- (b) II > III > I > IV
- (c) II > I > IV > III
- (d) none of these.
- 3. Chlorobenzene reacts with Mg in dry ether to give a compound (*A*) which further reacts with ethanol to yield
  - (a) phenol
- (b) benzene
- (c) ethylbenzene
- (d) ethyl phenyl ether.
- 4. Among the following compounds which can be dehydrated very easily is



Compound (X) is

6. Toluene reacts with excess of Cl<sub>2</sub> in presence of sunlight to give a product which on hydrolysis followed by reaction with NaOH gives



7. The aerial oxidation of chloroform in sunlight to phosgene can be checked by

- (a) keeping chloroform in coloured bottles but not completely filled
- (b) adding a few drops of 1% C<sub>2</sub>H<sub>5</sub>OH
- (c) adding a few drops of dil. HCl or NaOH
- (d) both (a) and (b).
- 8. Which one of the following compounds has the most acidic nature?

9. Consider the following sequence of reactions

$$\begin{array}{ccc} \operatorname{CH}_{3} - \operatorname{CH} - \operatorname{CH}_{3} & \xrightarrow{\operatorname{PBr}_{3}} X & \xrightarrow{\operatorname{Mg/ether}} Y \\ & & & & & & & \\ \operatorname{OH} & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & &$$

The final product Z is

10. Which of the following reagent is most suitable for the following conversion?

Ph Ph OH

$$CH_3$$
— $CH=CH_2$ — $?$   $CH_3$ — $CH_3$ — $CH_3$ 
 $CH_3$ 

- (a)  $H^+/HO-R$
- (b) TsCl, ROH
- (c) Hg(OCOCF<sub>3</sub>)<sub>2</sub>, ROH, NaBH<sub>4</sub>
- (d)  $B_2H_6/THF$ ,  $H_2O_2/OR^-$ .
- 11. Methyl alcohol can be distinguished from ethyl alcohol using
  - (a) sodium hydroxide and iodine
  - (b) Schiff's reagent
  - (c) Fehling solution
  - (d) phthalein fusion test.

12. Consider the structures of the following two molecules:

$$X: F_2C = C = CF_2$$

$$Y: F_2B - C \equiv C - BF_2$$

In which of these two, it is impossible for all the four F-atoms to lie in the same plane?

- (a) X
- (b) Y
- (c) Both *X* and *Y*
- (d) None of these

#### **Assertion & Reason Type**

**Directions**: In the following questions, a statement of assertion is followed by a statement of reason. Mark the correct choice as:

- (a) If both assertion and reason are true and reason is the correct explanation of assertion.
- (b) If both assertion and reason are true but reason is not the correct explanation of assertion.
- (c) If assertion is true but reason is false.
- (d) If both assertion and reason are false.
- 13. Assertion: Both symmetrical and unsymmetrical ethers can be prepared by Williamson's synthesis.

  Reason: Williamson's synthesis is an example of nucleophilic substitution reaction.
- **14. Assertion**: Alkyl halides form alkenes when heated above 300°C.

**Reason**: CH<sub>3</sub>CH<sub>2</sub>I reacts slowly with strong base than compared to CD<sub>3</sub>CH<sub>2</sub>I.

**15. Assertion** : Anisole undergoes electrophilic substitution at *o*- and *p*-positions.

**Reason**: Anisole is less reactive than phenol towards electrophilic substitution reactions.

#### Solution Senders of Chemistry Puzzle July 2019

- Esha Bhattacharya, West Bengal
- Swapnil Negi, Gujarat
- Devjit Acharjee, West Bengal
- Mohammad Arman UI Haque, Uttar Pradesh
- Shailaja Tekaday, Maharashtra
- Debasish Kalita, Assam
- Ashish Singh, Dadar & Nagar Haveli
- Renuka Kale, Maharashtra

#### Solution Senders of Chemistry Musing

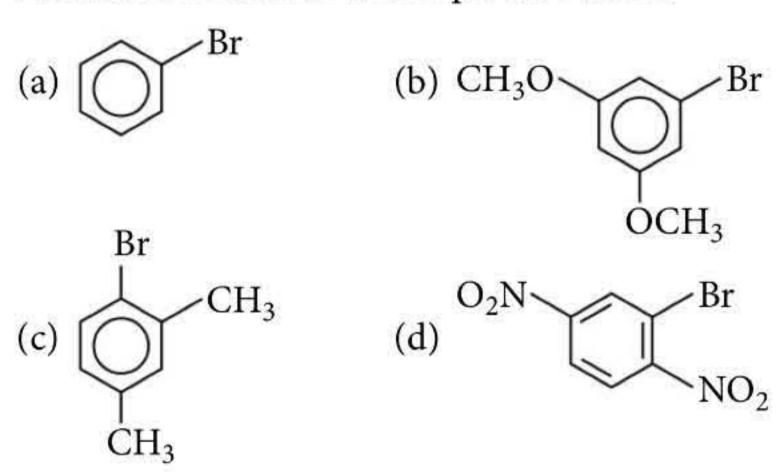
Set - 72

- Ajay Rathore, Maharashtra
- Shweta Singh, Uttar Pradesh

#### **JEE MAIN / ADVANCED**

#### Only One Option Correct Type

- **16.** In the conversion of *p*-nitrofluorobenzene to *p*-nitroanisole, intermediate *X* is involved.
  - the intermediate is aromatic.
  - (II) the intermediate is resonance stabilized anion.
  - (III) electron withdrawing group on the benzene ring stabilize the intermediate.
  - Only II and III
- (b) Only II
- Only I and III
- (d) Only I
- 17. An optically active, pure, four carbon containing saturated alcohol X when reacted with NaH followed by  $CH_3$  – I gives a compound M. Same alcohol (X) when treated with TsCl followed by sodium methoxide gives M'. M and M' are
  - (a) identical
- (b) enantiomers
- diastereomers
- (d) geometrical isomers.
- 18. Which of the following compounds is the most likely to undergo a bimolecular nucleophilic substitution reaction with aqueous NaOH?



19. Consider the following reactions carried out at the same temperature.

(i) 
$$O \longrightarrow \frac{H_2SO_4}{\text{in CH}_3CN}$$
  
(ii)  $O \longrightarrow \frac{H_2SO_4}{\text{in CH}_3CN}$ 

Which of the following statement is correct about these reactions?

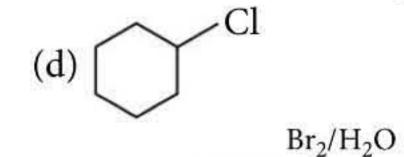
- (a) Both the reactions take place at the same rate.
- (b) The first reaction takes place faster than second reaction.
- (c) The second reaction takes place faster than first reaction.
- (d) Both the reactions take place by S<sub>N</sub>1 mechanism.

#### More than One Options Correct Type

20. Propan-1-ol and Propan-2-ol can be distinguished by

- (a) oxidation with alkaline KMnO<sub>4</sub> followed by reaction with H<sub>2</sub>O
- (b) oxidation with PCC followed by reaction with Tollens' reagent
- (c) oxidation by heating with copper followed by reaction with iodoform test
- (d) reaction with conc. H<sub>2</sub>SO<sub>4</sub> followed by reaction with Fehling solution.
- 21. Which of the following alkyl halides gives the same product in both  $S_N1$  and  $S_N2$  reactions?
  - (a) (R)— $CH_3CHBrCH_2CH_3$

(c) (S)-
$$C_6H_5$$
- $CH$  $<$ Br



 $\rightarrow$  (Y)C<sub>6</sub>H<sub>3</sub>O<sub>2</sub>Br<sub>3</sub> (X)22. Aromatic CHCl<sub>3</sub>/NaOH/ $\Delta$ > (Z)

The correct statements are

(a) (X) is an aromatic acid

OH(b) (*Z*) can be HO

- (c) (Y) on heating with Zn forms symmetrical tribromobenzene
- (d) (X) can be obtained by fusion of benzene-1, 3-disulphonic acid with NaOH.



23. Which of the following order is/are correct for the solvolysis in 50% aqueous ethanol at 44.6 °C?

(a) 
$$\nearrow$$
 Cl  $<$  Cl  $<$ 

#### Numerical Value Type

24. How many of the following reactions involved  $S_N$ 2 attacks?

(i) aq. NaN<sub>3</sub> (i) aq. NaCN (i) Li(Al)D<sub>4</sub> aq. HCl (i) EtSH (ii) 
$$SnCl_2 + HCl$$
 (ii)  $H_2O$  (ii)  $H_2O$  (ii)  $OH$  (ii)  $OH$  (ii)  $OH$  (ii)  $OH$  (iii)  $OH$ 

- 25. A 10 g mixture of iso-butane and iso-butene requires 20 g of Br<sub>2</sub> (in CCl<sub>4</sub>) for complete addition. If 10 g of the mixture is catalytically hydrogenated and the entire alkane is monobrominated in the presence of light at 127 °C, then how much monobrominated product would be formed?
- 26. The number of pentyl alcohol producing blue colouration in the Victor-Meyer's test is

#### Matrix Match Type

Answer the following questions (27 and 28) by appropriately matching the columns based on the information given in the passage.

A number of polyhalogen compounds e.g., dichloromethane chloroform, iodoform, freons and DDT have many industrial applications. However some of these compounds cannot be easily decomposed and even cause depletion of ozone layer and are proving environmental hazards.

.....

#### Column-I

#### Column-II

- Iodoform
- 1. CF<sub>4</sub>
- **BHC**
- 2. Antiseptic
- Freon-14
- 3. Moth repellent
- Halothanes
- 4. Inhalative anaesthetic
- E. *p*-Dichlorobenzene 5. Termite pesticide
- Which of the following has the correct combination considering Column-I and Column-II?
  - (a) A-5
- (b) B-2
- (c) C-4
- (d) E-3
- Which of the following has the correct combination considering Column-I and Column-II?
  - (a) A-3
- (b) B-5
- (c) C-2
- (d) D-1

Answer the following questions (29 and 30) by appropriately matching the column based on the information given in the passage.

Primary, secondary and tertiary alcohols can be distinguished from one another by different methods and techniques like oxidation, action of heated copper, Victor Meyer test and Lucas test etc. Same way different tests are being used to distinguish between alcohols, phenols and ethers with each other.

#### Column-I

#### Column-II

- A. Methanol and ethanol
- 1. Lucas reagent
- Phenol and cyclohexanol
- 2. Sodium metal
- C. *n*-Butyl alcohol and 3. Iodoform test *t*-butyl alcohol
- Methanol and diethyl ether
- 4. Ferric chloride
- Which of the following has the correct combination considering Column-I and Column-II?
  - (a) A-3
- (b) B-1
- (c) C-2
- (d) D-4
- 30. Which of the following has the correct combination considering Column-I and Column-II?
  - (a) A-2
- (b) B-4
- (c) C-3
- (d) D-1



Keys are published in this issue. Search now! ©



#### Check your score! If your score is

GOOD WORK! 90-75% 74-60%

< 60%

**EXCELLENT WORK!** You are well prepared to take the challenge of final exam. You can score good in the final exam.

**SATISFACTORY!** 

You need to score more next time.

NOT SATISFACTORY! Revise thoroughly and strengthen your concepts.

## CHEMISTRY MUSING

PROBLEM **SET 73** 

Themistry Musing was started from August '13 issue of Chemistry Today. The aim of Chemistry Musing is to augment the J chances of bright students preparing for JEE (Main and Advanced) / NEET / AIIMS / JIPMER with additional study material. In every issue of Chemistry Today, 10 challenging problems are proposed in various topics of JEE (Main and Advanced) / NEET. The detailed solutions of these problems will be published in next issue of Chemistry Today.

The readers who have solved five or more problems may send their solutions. The names of those who send atleast five correct solutions will be published in the next issue. We hope that our readers will enrich their problem solving skills through "Chemistry Musing" and stand in better stead while facing the competitive exams.

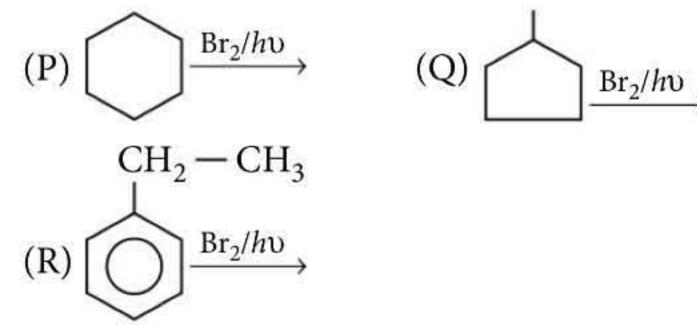
#### JEE MAIN/NEET

0.1 M solution of KI reacts with excess of H<sub>2</sub>SO<sub>4</sub> and KIO<sub>3</sub> solutions, according to equation:

$$5I^{-} + IO_{3}^{-} + 6H^{+} \rightarrow 3I_{2} + 3H_{2}O$$

Which of the following statements is incorrect?

- (a) 200 mL of the KI solution reacts with 0.004 mole of KIO<sub>3</sub>.
- (b) 100 mL of the KI solution reacts with 0.006 mole of  $H_2SO_4$ .
- (c) 0.5 litre of KI solution produce 0.05 mole of  $I_2$ .
- (d) Equivalent weight of KIO<sub>3</sub> is equal to Molecular weight
- Which of the following statements are correct?
  - 1. The increasing order of osmotic pressure of 0.1 M aqueous solution containing different electrolyte is as follows:
    - 0.1 M Glucose < 0.1 M NaCl < 0.1 MgCl<sub>2</sub>
  - Density of a solution is independent of temperature.
  - Camphor has comparatively larger value of  $K_f$ as compared to other common solvents.
  - 4. Limiting value of van't Hoff factor of  $K_4$ Fe(CN)<sub>6</sub> is 11.
  - (a) Only 1 and 2 (b) Only 1 and 3
- - (c) Only 1, 2 and 4 (d) All of these
- 3. Among the following free radical bromination reactions. Select those in which 2° halide is the major product.



(S) 
$$\xrightarrow{Br_2/h\upsilon}$$
 (T)  $\xrightarrow{Br_2/h\upsilon}$ 

- $Br_2/h\upsilon$
- (a) P, Q, R, S
- (b) P, R, U
- (c) P, R, S, T
- (d) P, Q, R, S, T
- Which of the reactions is/are correct to get cinnamic acid?
  - 1.  $C_6H_5CH = O \xrightarrow{(CH_3CO)_2 O/CH_3COONa}$
  - 2.  $C_6H_5CH = O \xrightarrow{CH_2(COOC_2H_5)_2} Pyridine$
  - 3.  $C_6H_5CH = O \frac{CH_3COOC_2H_5/OH^2}{2}$
  - 4.  $C_6H_5CH = O \xrightarrow{(i) BrCH_2 COOC_2H_5/Zn/\Delta} (ii) H_2O/H^+/\Delta$

  - (a) Only 1 and 3 (b) Only 1, 2 and 4

  - (c) Only 1 and 4 (d) Only 1, 3 and 4
- Addition of KI to a solution of [Ag(NH<sub>3</sub>)<sub>2</sub>]NO<sub>3</sub> precipitates AgI but no precipitate of Ag is formed when KI is added to a solution of K[Ag(CN)<sub>2</sub>] of same molar concentration as that of ammine complex. If the instability constants of the two complexes be  $k_1$  and  $k_2$  respectively, then

  - (a)  $k_1 > k_2$  (b)  $k_1 = k_2$

  - (c)  $k_1 < k_2$  (d)  $k_1 > 2k_2$

#### **JEE ADVANCED**

In the given reaction, mention reaction mechanism respectively

$$CH_3$$
  $CH_3$   $CH_3$ 
(I)  $H \stackrel{}{\longleftarrow} Br \longrightarrow H \stackrel{}{\longleftarrow} C_6H_{13}$  OH

(II) 
$$CH_3 \xrightarrow{C_2H_5} Br \longrightarrow CH_3 \xrightarrow{H} OH + CH_3 \xrightarrow{H} OH$$
  
 $H$   $C_2H_5$ 

(III) 
$$H \xrightarrow{CH_3} H \xrightarrow{CH_3} H \xrightarrow{CI} C_2H_5$$

- (a)  $S_N 2$ ,  $S_N 1$ ,  $S_N 2$  (b)  $S_N 2$ ,  $S_N 1$ ,  $S_N i$  (c)  $S_N 1$ ,  $S_N 2$ ,  $S_N i$  (d)  $S_N 2$ ,  $S_N i$ ,  $S_N 1$

#### COMPREHENSION

A (Yellow or orange colour)

$$Ti(SO_4)_2/H^+$$
 $E + D \leftarrow Cl_2$ 
 $X$ 

Absorbed in pyragallol

 $KI/Starch$ 

Blue solution (C)

- Identify compound *X*.
  - (a)  $MnO_2$
- (b)  $K_2Cr_2O_7$
- (c)  $H_2O_2$
- (d)  $Cl_2O_7$
- If *B* is allowed to react with *D*, a gas is formed. If this gas is passed through *X*, again *D* and *E* are formed. The compound *B* and *D* are
  - (a)  $K_2MnO_4$ ,  $Cl_2$
- (b) MnO<sub>2</sub>, HCl
- (c)  $K_2MnO_4$ , HCl
- (d)  $MnO_2$ ,  $Cl_2$

#### **NUMERICAL VALUE**

- A sample weighing 2.198 g containing a mixture of AO and  $A_2O_3$  takes 0.015 mole of  $K_2Cr_2O_7$  to oxidise the sample completely to form  $AO_4^-$  and  $Cr^{3+}$ . If 0.0187 mole of  $AO_4^-$  is formed, what is atomic weight of *A*?
- 10. Examine the structural formulas given below and identify the number of compound which are reduced by NaBH<sub>4</sub>.

$$\bigcap_{H, \bigcap_{NH_{2,}}} O$$

$$\frac{1}{\sqrt{1}}$$
,  $\frac{1}{\sqrt{1}}$ 

$$O$$
 $N-H$ 

#### IIT researchers find "solution" to oil spills

IIT Delhi may have found a solution to the menace of oil spilling. A team of researchers at the institute have developed a hydrophobic material that can separate oil from water and help in extracting the oil out. The material developed by IIT in the past few months attaches to the oil molecules and turns it magnetic; easy enough for the oil to be removed by a magnet.

According to IIT Delhi due to a rapid increase in use and transport of oils over the years, oil spillage and leakage accidents are occurring frequently worldwide.

The pollution by oil leaks contains many hazardous molecules including aromatic hydrocarbons and cyclo-paraffins, hence the removal of oil spilled over water and has become an important issue for protecting the environment.

To deal with this pollution with oil leaks, IIT Delhi researchers Neeraj Khare and Sandeep Munjal have come out with an invention "that relates to a novel reusable and stable super-hydrophobic (repelling water) and super-oleophilic (affinity to oil) carbon based nanocomposite for efficient separation of oils from oil-water mixture.

Khare, speaking to TOI explained that the carbon fibre based nanocomposite developed by IIT-Delhi has low density porous structure and has been synthesized in natural cotton with embedded magnetic nanoparticles.

"Because of that it quickly absorbs oil but does not absorb water. When introduced in the oil spillage on water, the product absorbs oil drops instantaneously. And since it is magnetic in nature the nanocomposite material can be used to remove oil from the oil-water mixture making very efficient to remove oil spilled over the water surface on a large area," Khare said.

He added that since the nanocomposite is synthesised from cotton, it is porous and spongy nature, "so the soaked oil can be extracted from it by just squeezing it and it can be reused."

Khare stated that in the last few years, there have occurred many large oil spill incidents throughout the world, including Montara oil spill of Australia, Deep water horizon at the Gulf of Mexico and the Xingang Port oil spill were the most alarming.

"The marine atmosphere is the most affected due to such incidents, and the spill may have impact on marine life in many ways and kill the fishes. Oil spilled over water floats like a mat on the water's surface with the thick sludge, which reduce oxygen levels in the water and prevents the penetration of sunlight into the water." Due to all these challenges and issues, the removal of oil spilled over water and other organic chemical leakage in water has become an important issue "and our invention of carbon based nanocomposite can provide effective solution to this problem," the researcher who has been working on the invention for several months, claimed.

He informed that a major oil spill that took place in Chennai on January 28, 2017, and it took weeks to remove the sludge that spread along the coastline. "If our nanocomposite was available back then, the impact of the oil spillage would ahvr been minimal as we could have used large quantities of it to to absorb the oil instantaneously," he claimed.

IIT-Delhi has already patented the product with the government of Indian and will be approaching the government and members of the industry to acquire their invention and utilize them.

Courtesy: The Times of India



#### **CATEGORY-I (Q. 1 to Q. 30)**

Carry 1 mark each and only one option is correct. In case of incorrect answer or any combination of more than one answer, ¼ mark will be deducted.

1. One of the products of the following reaction is *P*.

$$CCl_3 \xrightarrow{\text{(i) aq. KOH}} P$$

Structure of *P* is

(a) 
$$CO_2H$$
 (b)  $HO$   $CI$   $CI$ 

2. For the reaction below, the product is Q.

HO
$$CO_2H$$

Acetic anhydride
 $Q[C_9H_8O_4]$ 

Conc.  $H_2SO_4(cat.)$  heat

The compound *Q* is

(a) 
$$CO_2H$$
  $COOCOCH_3$   $OH$   $COOCOCH_3$   $OH$   $CO_2H$   $COCH_3$   $COCH_3$   $COCH_3$   $COCH_3$   $COCH_3$   $COCH_3$   $COCH_3$   $COCH_3$ 

- 3. Cyclopentanol on reaction with NaH followed by CS<sub>2</sub> and CH<sub>3</sub>I produces a/an
  - (a) ketone
- (b) alkene
- (c) ether
- (d) xanthate.

- 4. The compound, which evolves carbon dioxide on treatment with aqueous solution of sodium bicarbonate at 25°C, is
  - (a)  $C_6H_5OH$
- (b) CH<sub>3</sub>COCl
- (c) CH<sub>3</sub>CONH<sub>2</sub>
- (d) CH<sub>3</sub>COOC<sub>2</sub>H<sub>5</sub>
- 5. The indicated atom is not a nucleophilic site in
  - (a) BH<sub>4</sub>
- (b) CH<sub>3</sub>MgI
- (c) CH<sub>3</sub> H
- (d) CH<sub>3</sub>NH<sub>2</sub>
- 6. The charge carried by 1 millimole of  $M^{n+}$  ions is 193 coulombs. The value of n is
  - (a) 1
- (b) 2
- (c) 3
- (d) 4
- 7. Which of the following mixtures will have the lowest pH at 298 K?
  - (a) 10 mL 0.05 N CH<sub>3</sub>COOH + 5 mL 0.1 N NH<sub>4</sub>OH
  - (b) 5 mL 0.2 N NH<sub>4</sub>Cl + 5 mL 0.2 N NH<sub>4</sub>OH
  - (c)  $5 \text{ mL } 0.1 \text{ N CH}_3\text{COOH} +$

10 mL 0.05 N CH<sub>3</sub>COONa

- (d) 5 mL 0.1 N CH<sub>3</sub>COOH + 5mL 0.1 N NaOH
- **8.** Consider the following two first order reactions occurring at 298 K with same initial concentration of *A*:
  - (1)  $A \rightarrow B$ ; rate constant,  $k = 0.693 \text{ min}^{-1}$
  - (2)  $A \rightarrow C$ ; half-life,  $t_{1/2} = 0.693$  min Choose the correct option.
  - (a) Reaction (1) is faster than reaction (2).
  - (b) Reaction (1) is slower than reaction (2).
  - (c) Both reactions proceed at the same rate.
  - (d) Since two different products are formed, rates cannot be compared.
- 9. For the equilibrium,  $H_2O_{(l)} \rightleftharpoons H_2O_{(v)}$ , which of the following is correct?
  - (a)  $\Delta G = 0$ ,  $\Delta H < 0$ ,  $\Delta S < 0$
  - (b)  $\Delta G < 0$ ,  $\Delta H > 0$ ,  $\Delta S > 0$
  - (c)  $\Delta G > 0$ ,  $\Delta H = 0$ ,  $\Delta S > 0$
  - (d)  $\Delta G = 0$ ,  $\Delta H > 0$ ,  $\Delta S > 0$

- 10. For a van der Waals' gas, the term  $\left(\frac{ab}{V^2}\right)$  represents some
  - (a) pressure
- (b) energy
- (c) critical density
- (d) molar mass.
- 11. In the equilibrium,  $H_2 + I_2 \rightleftharpoons 2HI$ , if at a given temperature the concentrations of the reactants are increased, the value of the equilibrium constant,  $K_c$ , will
  - (a) increase
- (b) decrease
- remain the same
- (d) cannot be predicted with certainty.
- 12. If electrolysis of aqueous CuSO<sub>4</sub> solution is carried out using Cu-electrodes, the reaction taking place at the anode is
- (a)  $H^+ + e^- \to H$  (b)  $Cu^{2+}_{(aq)} + 2e^- \to Cu_{(s)}$ (c)  $SO^{2-}_{4(aq)} 2e^- \to SO_4$  (d)  $Cu_{(s)} 2e^- \to Cu^{2+}_{(aq)}$
- 13. Which one of the following electronic arrangements is absurd?
  - (a) n = 3, l = 1, m = -1 (b) n = 3, l = 0, m = 0

  - (c) n = 2, l = 0, m = -1 (d) n = 2, l = 1, m = 0
- 14. The quantity  $hv/k_B$  corresponds to
  - (a) wavelength
- (b) velocity
- (c) temperature
- (d) angular momentum.
- 15. In the crystalline solid  $MSO_4.nH_2O$  of molar mass 250 g mol<sup>-1</sup>, the percentage of anhydrous salt is 64 by weight. The value of *n* is
  - (a) 2
- (b) 3
- (c) 5
- (d) 7
- 16. At S.T.P. the volume of 7.5 g of a gas is 5.6 L. The gas is
  - (a) NO

- (b)  $N_2O$  (c) CO (d)  $CO_2$
- 17. The half-life period of  $_{53}I^{125}$  is 60 days. The radioactivity after 180 days will be
  - (a) 25%
- (b) 12.5% (c) 33.3% (d) 3.0%

- 18. Consider the radioactive disintegration

 $_{82}A^{210} \rightarrow B \rightarrow C \rightarrow _{82}D^{206}$ 

The sequence of emission can be

- (a)  $\beta$ ,  $\beta$ ,  $\beta$  (b)  $\alpha$ ,  $\alpha$ ,  $\beta$  (c)  $\beta$ ,  $\beta$ ,  $\gamma$  (d)  $\beta$ ,  $\beta$ ,  $\alpha$
- 19. The second ionisation energy of the following elements follows the order

  - (a) Zn > Cd < Hg (b) Zn > Cd > Hg

  - (c) Cd > Hg < Zn (d) Zn < Cd < Hg
- 20. The melting point of (i) BeCl<sub>2</sub> (ii) CaCl<sub>2</sub> and
  - (iii) HgCl<sub>2</sub> follows the order

(a) i < ii < iii

- (b) iii < i < ii
- (c) i < iii < ii
- (d) ii < i < iii
- 21. Which of these species will have non-zero magnetic moment?
  - (a) Na<sup>+</sup>
- (b) Mg
- (c) F
- (d) Ar<sup>+</sup>

- 22. The first electron affinity of C, N and O will be of the order

  - (a) C < N < O (b) N < C < O
  - (c) C < O < N (d) O < N < C
- 23. The H—N—H angle in ammonia is 107.6°, while the H—P—H angle in phosphine is 93.5°. Relative to phosphine, the *p*-character of the lone pair on ammonia is expected to be
  - (a) less
- (b) more
- (c) same
- (d) cannot be predicted.
- **24.** The reactive species in chlorine bleach is
  - (a) Cl<sub>2</sub>O (b) OCl<sup>-</sup> (c) ClO<sub>2</sub>

- (d) HCl
- 25. The conductivity measurement of a coordination compound of cobalt (III) shows that it dissociates into 3 ions in solution. The compound is
  - (a) hexaamminecobalt(III) chloride
  - (b) pentaamminesulphatocobalt(III) chloride
  - (c) pentaamminechloridocobalt(III) sulphate
  - (d) pentaamminechloridocobalt(III) chloride.
- 26. In the Baeyer's process, the leaching of alumina is done by using
  - (a) Na<sub>2</sub>CO<sub>3</sub> (b) NaOH (c) SiO<sub>2</sub>

- 27. Which atomic species cannot be used as a nuclear fuel?

  - (a)  $^{233}_{92}U$  (b)  $^{235}_{92}U$  (c)  $^{239}_{94}Pu$  (d)  $^{238}_{92}U$
- 28. The molecule/molecules that has/have delocalised lone pair(s) of electrons is/are

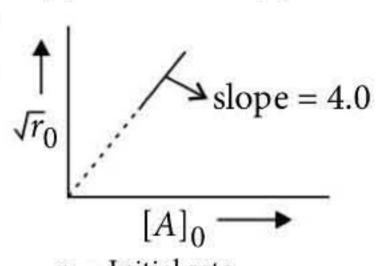
- (IV)  $CH_3CH = CHCH_2NHCH_3$
- (a) I, II and III
- (b) I, II and IV
- (c) I and III
- (d) only III
- **29.** The conformations of *n*-butane, commonly known as eclipsed, gauche and anti-conformations can be interconverted by
  - (a) rotation around C—H bond of a methyl group
  - (b) rotation around C—H bond of a methylene group
  - (c) rotation around C1—C2 linkage
  - (d) rotation around C2—C3 linkage.

- 30. The correct order of the addition reaction rates of halogen acids with ethylene is
  - (a) hydrogen chloride > hydrogen bromide > hydrogen iodide
  - (b) hydrogen iodide > hydrogen bromide > hydrogen chloride
  - (c) hydrogen bromide > hydrogen chloride > hydrogen iodide
  - (d) hydrogen iodide > hydrogen chloride > hydrogen bromide.

#### CATEGORY-II (Q. 31 to Q. 35)

Carry 2 marks each and only one option is correct. In case of incorrect answer or any combination of more than one answer, ½ mark will be deducted.

- 31. The total number of isomeric linear dipeptides which can be synthesized from racemic alanine is
  - (a) 1
- (b) 2
- (c) 3
- (d) 4
- 32. The kinetic study of a reaction like  $\nu A \rightarrow P$ at 300 K provides the  $\sqrt{r_0}$ following curve, where concentration is taken in mol dm<sup>-3</sup> and time in min.

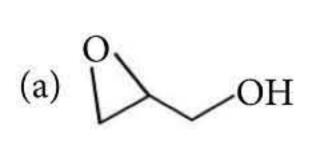


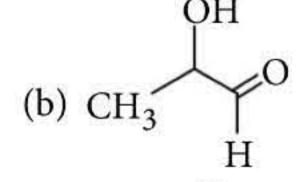
 $r_0$  = Initial rate  $[A]_0$ : Initial concentration of A

Identify the correct order (n) and rate constant (k).

- (a) n = 0,  $k = 4.0 \text{ mol dm}^{-3} \text{ min}^{-1}$
- (b) n = 1/2,  $k = 2.0 \text{ mol}^{1/2} \text{ dm}^{-3/2} \text{ min}^{-1}$
- (c)  $n = 1, k = 8.0 \text{ min}^{-1}$
- (d) n = 2,  $k = 16.0 \text{ dm}^3 \text{ mol}^{-1} \text{ min}^{-1}$
- 33. At constant pressure, the heat of formation of a compound is not dependent on temperature, when
  - (a)  $\Delta C_p = 0$  (b)  $\Delta C_V = 0$  (c)  $\Delta C_p > 0$  (d)  $\Delta C_p < 0$
- 34. A copper coin was electroplated with Zn and then heated at high temperature until there is a change in colour. What will be the resulting colour?

  - (a) White (b) Black (c) Silver
- (d) Golden
- 35. Oxidation of allyl alcohol with a peracid gives a compound of molecular formula C<sub>3</sub>H<sub>6</sub>O<sub>2</sub>, which contains an asymmetric carbon atom. The structure of the compound is





(c) 
$$H_3C \longrightarrow OF$$

#### CATEGORY-III (Q. 36 to 40)

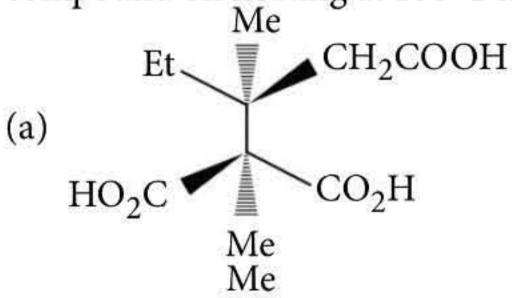
Carry 2 marks each and one or more option(s) is/are correct. If all correct answers are not marked and also no incorrect answer is marked then score =  $2 \times \text{number of correct answers}$ marked + actual number of correct answers. If any wrong option is marked or if any combination including a wrong option is marked, the answer will considered wrong, but there is no negative marking for the same and zero mark will be awarded.

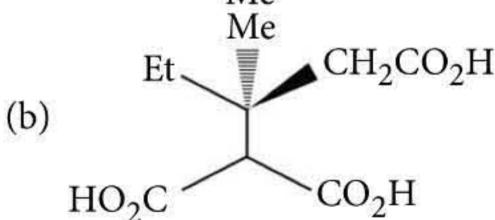
**36.** Haloform reaction with I<sub>2</sub> and KOH will be responded by

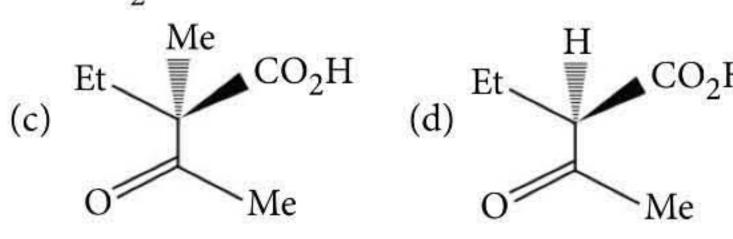
- **37.** Identify the correct statement(s).
  - (a) The oxidation number of Cr in  $CrO_5$  is +6.
  - (b)  $\Delta H > \Delta U$  for the reaction,  $N_2O_{4(g)} \rightarrow 2NO_{2(g)}$ , provided both gases behave ideally.
  - (c) pH of 0.1 N H<sub>2</sub>SO<sub>4</sub> is less than that of 0.1 N HCl at 25°C.

(d) 
$$\left(\frac{RT}{F}\right) = 0.0591 \text{ volt at } 25^{\circ}\text{C}$$
.

- 38. Compounds with spin-only magnetic moment equivalent to five unpaired electrons are
  - (a)  $K_4[Mn(CN)_6]$
- (b)  $[Fe(H_2O)_6]Cl_3$ 
  - (c)  $K_3[FeF_6]$
- (d)  $K_4[MnF_6]$
- 39. Which of the following chemicals may be used to identify three unlabelled beakers containing conc. NaOH, conc. H<sub>2</sub>SO<sub>4</sub> and water?
  - (a)  $NH_4NO_3$
- (b) NaCl
- (c)  $(NH_4)_2CO_3$
- (d) HCOONa
- **40.** The compound(s), capable of producing achiral compound on heating at 100°C is/are







#### SOLUTIONS

1. (c):
$$C = CCl_3 \xrightarrow{(i) \text{ aq. KOH}} CCCl_3 \xrightarrow{(ii) \text{ H}_3O^+} CCOOH$$

Benzoic acid

2. (a): 
$$\frac{\text{COOH}}{\text{conc. H}_2\text{SO}_4, \Delta}$$
HO

COOH

+ CH<sub>3</sub>COOH

+ CH<sub>3</sub>COOH

OH

OH

3. (d): 
$$NaH$$
  $S=C=S$ 

Cyclopentanol

$$O-C-\overline{SNa}^{+}$$

$$CH_{3}-\overline{I}$$

$$S=C=S$$

$$O-C-S-CH_{3}$$
(Xanthate)

(b): In aqueous NaHCO<sub>3</sub> solution, some amount of OH is present, which hydrolyses CH<sub>3</sub>COCl to CH<sub>3</sub>COOH which subsequently reacts with NaHCO<sub>3</sub> present in the medium to form  $CO_2$ .

(a): In  $BH_4^-$ , there is no lone pair on B-atom. Hence, it is not a nucleophilic site.

(b): Charge on 1000 millimoles (= 1 mole) of  $M^{n+}$  ions = 193 × 1000 C = 193000 C = 2 F Hence, n = 2

(c): CH<sub>3</sub>COOH + CH<sub>3</sub>COONa 0.1 N, 5 mL 0.05 N, 10 mL milli eq.

It is acidic buffer, pH =  $pK_a + log \frac{[CH_3COO^-]}{[CH_3COOH]}$  $pH = pK_a$ 

This solution will have lowest pH.

(b): For reaction (1):  $A \rightarrow B$ , rate constant  $(k_1) = 0.693 \text{ min}^{-1}$ For reaction (2),  $A \rightarrow C$ ,

rate constant 
$$(k_2) = \frac{0.693}{t_{1/2}} \Rightarrow \frac{0.693}{0.693} = 1 \text{ min}^{-1}$$

So,  $k_1 < k_2$ 

Hence, reaction (1) is slower than reaction (2).

(d):  $H_2O_{(l)} \rightleftharpoons H_2O_{(v)}$ 

As the process is in equilibrium,  $\Delta G = 0$ 

 $\Delta H > 0$  (as the process is endothermic)

 $\Delta S > 0$  (as entropy is increases from liquid to gas)

10. (b): For  $\frac{ab}{V^2}$ , a and b are van der Waals' constants.

Unit of 
$$a = \frac{\text{atm} \cdot \text{L}^2}{(\text{mole})^2}$$

Unit of 
$$b = \frac{L}{\text{mole}}$$

V = volume of gas per mole = L/mole

So, 
$$\frac{ab}{V^2} = \frac{\frac{\text{atm} \cdot \text{L}^2}{\text{(mole)}^2} \times \frac{\text{L}}{\text{mole}}}{\text{(L/mole)}^2} = \frac{\text{atm L}}{\text{mole}}$$

It is the unit of energy.

11. (c): The value of equilibrium constant for a particular reaction is always constant depending only upon the temperature of reaction and is independent of concentration of reactants.

12. (d): The reactions occurring at the electrodes are as follows:

At cathode:  $Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$ 

At anode:  $Cu_{(s)} \rightarrow Cu_{(aq)}^{2+} + 2e^{-}$ 

*i.e.*, copper dissolves into the solution from the anode and is deposited at the cathode.

13. (c) : Quantum number set n = 2, l = 0, m = -1 is not possible because for l = 0, value of m should be zero.

14. (c): 
$$K.E. = \frac{3}{2}k_BT = hv$$
 (for photon)  

$$\therefore \frac{hv}{k} \propto T$$

$$\therefore \frac{no}{k_B} \propto 7$$

15. (c) : Mass of anhydrous  $MSO_4$  salt

$$=\frac{64}{100} \times 250 = 160 \text{ g/mole}$$

Total mass of  $H_2O$  in  $MSO_4 \cdot nH_2O = 250 - 160$ = 90 g/mole

Therefore, the value of  $n = \frac{90}{18} = 5$ 

16. (a): 5.6 L at S.T.P weighs = 7.5 g

$$\therefore$$
 22.4 L at S.T.P weighs =  $\frac{7.5 \times 22.4}{5.6} = 30$ 

∴ Molar mass = 30 g/mol, which is the molar mass of NO.

17. (b): Radioactivity after time, t

$$(N_t) = \frac{N_0}{(2)^n}$$
 and  $n = \frac{t}{t^{1/2}}$ 

So, 
$$n = \frac{180}{60} = 3$$
;  $N_t = \frac{N_0}{(2)^3} = \frac{N_0}{8} = 0.125$ 

Hence, radioactivity after 180 days = 12.5%

18. (d): 
$$_{82}A^{210} \xrightarrow{-\beta} _{83}B^{210} \xrightarrow{-\beta} _{84}C^{210} \xrightarrow{-\alpha} _{82}D^{206}$$

Therefore, the sequence of emission will be  $\beta$ ,  $\beta$ ,  $\alpha$ .

19. (a)

21. (d): Number of unpaired electrons in

$$_{11}$$
Na<sup>+</sup> =  $1s^2 2s^2 2p^6 = 0$ 

$$_{12}$$
Mg =  $1s^22s^22p^63s^2 = 0$ 

$$_{9}F^{-} = 1s^{2}2s^{2}2p^{6} = 0$$

$$_{18}\mathrm{Ar^{+}}=1s^{2}2s^{2}2p^{6}3s^{2}3p^{5}=1$$

As only Ar<sup>+</sup> has one unpaired electron, so it has non-zero magnetic moment.

- **22. (b)** : Along a period, on moving from left to right, electron affinity increases due to increase in nuclear charge (*Z*) but N has less electron affinity than C as it has half-filled *p*-orbital (stable).
- 23. (a): As bond angle decreases, p-character increases.
- $\therefore$  Bond angle order : NH<sub>3</sub> > PH<sub>3</sub>
- p-character order :  $NH_3 < PH_3$
- **24. (b)** : Chlorine bleach is CaOCl<sub>2</sub>. Its composition is Ca<sup>2+</sup>, Cl<sup>-</sup>, OCl<sup>-</sup>.
- 25. (d): Pentaamminechloridocobalt(III) chloride i.e.,  $[Co(NH_3)_5Cl]Cl_2 \rightleftharpoons [Co(NH_3)_5Cl]^{2+} + 2Cl^{-3}$
- **26. (b)** : In Baeyer's process, powdered ore of alumina (bauxite) is heated with conc. NaOH.

$$Al_2O_3 + 2NaOH + 3H_2O \longrightarrow 2Na[Al(OH)_4]$$
  
 $2Na[Al(OH)_4] + 2CO_2 \longrightarrow Al_2O_3.xH_2O + 2NaHCO_3$   
 $Al_2O_3.xH_2O \xrightarrow{1470 \text{ K}} Al_2O_3 + xH_2O$ 

27. (d)

**28.** (d): In compound (III), the lone pair of oxygen gets delocalised on the  $\pi$ -bond located on the next carbon atom.

$$\bigcirc \ddot{\circ}_{-CH_3} \longleftrightarrow \bigcirc \ddot{\circ}_{-CH_3}$$

**29.** (d): Rotation around central C - C (C2 - C3), results in different conformations of n-butane.

60° ↑
Rotation Rotation

$$H_3C$$
 $H_3C$ 
 $H_3C$ 
 $H_3C$ 
 $H_3C$ 
 $H_3C$ 
 $H_3C$ 
 $H_3C$ 
 $H_3C$ 
 $H_4C$ 
 $H_5C$ 
 $H_5C$ 
 $H_5C$ 
 $H_7$ 
 $H_7$ 

**30. (b)**: As we go from HF to HI, bond strength decreases, therefore reactivity of halogen halides increases as: HI > HBr > HCl.

31. (d): 
$$H_2N \xrightarrow{Me} COOH + HOOC \xrightarrow{Me} NH_2$$
  
 $H$  (S-alanine)  $(R-alanine)$   $(S, S), (S, R), (R, R), (R, S)$ 

Therefore, number of possible dipeptides = 4

32. (d): From the graph, 
$$\sqrt{r_0} = 4[A]_0$$
 ...(i)  
Rate =  $k[A]_0^n$  ...(ii)

$$r_0 = 16 [A]_0^2$$
 ...(iii)

On comparing eq. (ii) and (iii), we get  $k = 16 \text{ dm}^3 \text{ mol}^{-1} \text{ min}^{-1}$ ; n = 2

33. (a): According to Kirchhoff's equation,  $\Delta H_2 = \Delta H_1 + \Delta C_p(\Delta T)$ 

when  $\Delta C_p = 0$  then  $\Delta H$  does not depend on temperature.

34. (d)

35. (a) : 
$$CH_2 = CH - CH_2 - OH \xrightarrow{[O]}$$
Allyl alcohol
$$CH_2 - \overset{\bullet}{C}H - CH_2 - OH$$

$$CH_2 - \overset{\bullet}{C}H - CH_2 - OH$$

$$CH_2 - \overset{\bullet}{C}H - CH_2 - OH$$

(a) I Ph 
$$I_2/KOH$$
 I O Ph  $I_2/KOH$  I O Ph  $I_3/KOH$  Ph  $I_3/KOH$  Ph  $I_3/KOH$  Ph  $I_3/KOH$  Ph  $I_3/KOH$  Ph  $I_3/KOH$  CH<sub>3</sub>

(b) 
$$N_2O_{4(g)} \rightarrow 2NO_{2(g)}$$
  
 $\Delta H = \Delta U + \Delta n_g RT$  ...(i)  
 $\Delta n_g = (2-1) = 1$ 

 $\therefore$  From eq. (i),  $\Delta H = \Delta U + RT$ 

 $\Delta H > \Delta U$ .

(c) For  $0.1 \text{ N H}_2\text{SO}_4$ ,  $[H^+] = 0.1 \text{ N}$ 

 $\therefore pH = 1$ 

For 0.1 N HCl,  $[H^+] = 0.1 \text{ N}$ 

 $\therefore$  pH = 1

Therefore, (c) is incorrect.

(d) 
$$\frac{RT}{F} = \frac{8.314 \times 298}{96500} = 0.0256 \text{ V}$$

Therefore, (d) is incorrect.

**38. (b, c, d)** : (a)  $K_4[Mn(CN)_6]$ ;  $Mn^{2+} = [Ar]3d^54s^0$   $CN^-$  is a strong field ligand, so, pairing will take place. i.e.,  $t_{2g}^{2,2,1} e_g^{0,0}$ 

(b)  $[\text{Fe}(\text{H}_2\text{O})_6]\text{Cl}_3$ ;  $\text{Fe}^{3+} = [\text{Ar}]3d^54s^0$   $\text{H}_2\text{O}$  is a weak field ligand, so, pairing will not occur. *i.e.*,  $t_{2g}^{1,1,1}e_g^{1,1}$ 

(c)  $K_3[FeF_6]$ ;  $Fe^{3+} = [Ar]3d^54s^0$   $F^-$  is a weak field ligand, so, pairing will not occur. *i.e.*,  $t_{2g}^{1,1,1} e_g^{1,1}$ 

(d)  $K_4[MnF_6]$ ;  $Mn^{2+}=[Ar]3d^54s^0$   $F^-$  is a weak field ligand so, pairing will not occur. *i.e.*,  $t_{2g}^{1,1,1}e_g^{1,1}$ 

Hence, (b), (c) and (d) complexes will show spin-only magnetic moment equivalent to five unpaired electrons.

(a) 
$$NH_4NO_3$$

$$\xrightarrow{conc. NaOH} NH_3 \uparrow + NaNO_3 + H_2O$$

$$\xrightarrow{conc. H_2SO_4} (NH_4)_2SO_4 + NO_2 \uparrow$$

$$+ O_2 + H_2O$$

$$\xrightarrow{water} No reaction$$

(c) 
$$(NH_4)_2CO_3$$

$$\xrightarrow{conc. NaOH} NH_3\uparrow + Na_2CO_3 + 2H_2O$$

$$\xrightarrow{conc. H_2SO_4} (NH_4)_2SO_4 + CO_2\uparrow + H_2O$$

$$\xrightarrow{water} No reaction$$

 $\mathrm{NH_3}$  is pungent smell gas,  $\mathrm{NO_2}$  is brown coloured gas,  $\mathrm{CO_2}$  is colourless, odourless gas (effervescence).  $\mathrm{NH_4NO_3}$  and  $\mathrm{(NH_4)_2CO_3}$  do not react with water.

40. (d):
$$\begin{array}{c}
H \\
COOH \\
O \end{array}$$

$$\begin{array}{c}
A \\
COO_2
\end{array}$$

$$\begin{array}{c}
H \\
Et \\
O \\
Me
\end{array}$$
Achiral

#### 2 crore additional seats in higher education by 2024

The government is striving to increase the number of seats in higher educational institutions by one-and-a-half times by 2024, President Ram Nath Kovind said on 20th June. Addressing the joint sitting of both the Houses of Parliament in the historic Central Hall, he said research is being encouraged in higher educational institutions and to strengthen this effort, there is a proposal to establish a 'National Research Foundation'. "This proposed foundation will work as a bridge between different Departments of the central government, science laboratories, higher educational institutions and industrial institutions," Kovind said. The president also said "Pradhan Mantri Innovative Learning Programme" will be started since it is the government's responsibility to provide appropriate opportunities, environment and quality education to enhance the talent of children. He said the government is striving to increase the number of seats in the country's higher education system by one-and-a-half times by 2024.

"With this initiative, two crore additional seats would be available for the youth in higher educational institutions. "To enable various higher educational institutions of India to find a place in the top 500 educational institutions of the world, they are being encouraged through grant of autonomy and financial assistance," he added. He also talked about how suitable infrastructure is being created to attract children early enough at the school level towards technology. "Through the 'Atal Innovation Mission', the work of establishing 'Atal Tinkering Labs' in about 9,000 schools across the country, is progressing rapidly. Similarly, 'Atal Incubation Centres' are being set up in 102 universities and other institutions," he said in his address.

The government has made provision of 10 per cent reservation for youth from economically weaker section of the general category which will enable them to get more opportunities in employment and education, the President said.



## CONCEPT BOSTER

Dear students!! Hope you all are fine. Don't forget that you are blazing stars. So keep shining. Keep the fire in you through paper education. Get in depth knowledge of every topic properly. Read the theory first and start practising. Always time yourself. This is best strategy for exam preparation. All the best.

\*Arunava Sarkar

#### ADVANCE APPROACH TO SOLVE NUMERICAL PROBLEMS

Numerical 1: A radioactive element decays by  $\beta$ -emission. Mass of parent nuclide is m and mass of daughter nuclide is m'. Calculate the energy liberated during the emission.

**Approach**: Change in mass  $(\Delta m) = m - m' - m_{\beta}$ Mass of  $\beta$  particle =  $m_{\beta}$ 

 $\therefore$  Energy liberated =  $\Delta m \cdot c^2 = (m - m' - m_{\beta}) c^2$ 

Numerical 2 : g

 $A \rightarrow nB$ 

At the point of intersection, find out the concentration of *B*.

**Approach**: Amount of [B] formed = Amount of [A] decayed  $\times n$ 

$$\therefore A_0 e^{-\lambda t} = A_0 (1 - e^{-\lambda t}) \times n \implies e^{-\lambda t} = \frac{n}{n+1}$$

(t = time after which we are calculating the amount of B)

$$\therefore [B]_{\text{formed}} = n \times A_0 \times (1 - e^{-\lambda t})$$
$$= n \times A_0 \times \left(1 - \frac{n}{n+1}\right) = \frac{nA_0}{n+1}$$

Numerical 3: For the first order opposed by first order reaction  $A \rightleftharpoons B$ . If we start with the concentration of A equal to 1 M, what will be the concentration of B in  $10^3/16$  min.  $K_f = 11 \times 10^{-3}$  min<sup>-1</sup>,  $K_b = 5 \times 10^{-3}$  min<sup>-1</sup>.

**Approach**: The integrated rate equation for this kind of problem is

$$\ln \frac{x_{eq}}{(x_{eq} - x)} = (K_f + K_b) t$$

$$\Rightarrow \ln \frac{x_{eq}}{x_{eq} - x} = 16 \times 10^{-3} \cdot t = 16 \times 10^{-3} \cdot \frac{10^3}{16} = 1 = \ln e$$

$$\therefore \frac{x_{eq}}{x_{eq} - x} = e \Rightarrow x = \frac{x_{eq}(e - 1)}{e}$$

$$\Rightarrow x = \left(\frac{2.718 - 1}{2.718}\right) \cdot x_{eq} = x_{eq} \times 0.632$$

$$A \rightleftharpoons K_f \Rightarrow B$$

$$1 \qquad 0$$

$$(1 - x_{eq}) \qquad x_{eq}$$

$$\therefore \frac{x_{eq}}{1 - x_{eq}} = \frac{K_f}{K_b} = \frac{11}{5} \Rightarrow 5x_{eq} = 11 - 11 x_{eq}$$

$$\Rightarrow 16x_{eq} = 11 \Rightarrow x_{eq} = \frac{11}{16}$$

$$\therefore x = \left(\frac{11}{16} \times 0.632\right) = 0.4345$$



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#### Dear Readers,

We have been receiving a lot of queries from students and their parents, so we decided to ease out you by introducing a new column to guide you through your worries, concerns and questions related to your studies and beyond. Readers can send their queries (concerns beyond specific subjects, career guidance, tips for better performance, etc.) by post or by email at editor@mtg.in. The solutions to your queries given by MTG experts will definitely ease your anxiety and provide you a clear vision and a right direction to achieve your goals. Best and most relevant questions will be chosen and published with the sender's name.

V For state admissions, through JEE Main 2020 eligibility is different or same? (Manisha, Punjab)

All candidates will have to qualify JEE Main 2020 examination for state admissions. However, the eligibility criteria will vary according to the state authorities.

V I am a mother of a Class 12<sup>th</sup> student. My son is an average student and he is not able to study for long hours. Please suggest some books which will help him to get good marks in CBSE Board?

(Sonia Tarachandwani, Delhi)

We would suggest your ward to go through NCERT Textbooks thoroughly first, then study NCERT Exemplar Solutions (MTG) because many questions in CBSE Board exams are asked from NCERT books.

Then the best way to get good marks in board exams is to study previous years' question papers thus our CBSE Champion will help a lot. CBSE Champion is chapterwise and topicwise so, it will be highly useful for unit tests as well.

V How do I study all the Organic Chemistry of Class 12th?

(Girish Purohit, Uttar Pradesh)

Organic Chemistry is very important as it offers lots of future opportunities but this subject is little difficult hence needs little attention, concentration and practice.

For better understanding of Organic Chemistry, you need to focus more on basics like mechanisms, reagents and reaction conditions. The most important thing is DO NOT MEMORISE. Try to understand how reactions proceed *i.e.* focus on the complete mechanism of the reactions.

From exam point of view, you should know the weightage of each chapter and the way questions are being asked. Practice complete NCERT exercises. Also, MTG books like CBSE Champion (for previous years' questions), Excel in Chemistry (for practice) and Score More (21 very similar practice papers) will help you a lot.

V I am a student of Class 12<sup>th</sup> and I am preparing for board as well as for various competitive exams. Can your monthly magazines help me in preparation?

(Shiven Singh, Maharashtra)

Yes, most definitely. Magazines are especially designed for the students who are preparing for board as well as for various medical or engineering entrance examinations. As our magazines contain topicwise theory, various questions from NEET to JEE Advanced level and practice papers for various exams so these will help you tremendously.

Magazines will also help you stay updated and well aware about the exam pattern and types of questions asked in various exams.

You will also get solved question papers for medical and engineering exams.

V Which chapters of Class 11<sup>th</sup> Chemistry are important for Class 12<sup>th</sup>?

(Jatin Munjal, Maharashtra)

Class 11<sup>th</sup> syllabus is very important as this makes your base strong.

In Organic Chemistry, "Some Basic Principles and Techniques of Organic Chemistry" is a very important chapter because this is the base of whole Organic Chemistry. It will help you to understand different mechanisms, reagents and reactions given in chapters of class XII.

In Inorganic Chemistry, "Classification of Elements and Periodicity in Properties and Chemical Bonding" are very important chapters. As you will require concepts of periodicity and bonding throughout Inorganic Chemistry of class XII.

In Physical Chemistry, few concepts like ideal gas equation (States of Matter), idea of spontaneity and laws of thermodynamics, concentration terms (Some Basic Concepts of Chemistry) and Redox Reactions are very important to easily grasp chapters of class XII.

All the Best

## Rank Enhancer

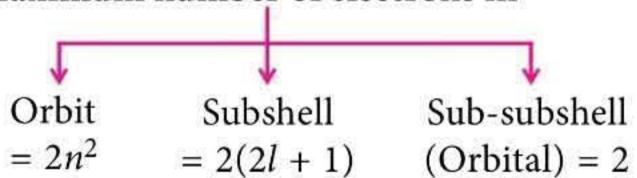
#### QUANTUM NUMBERS

Set of four numbers that are used to locate an electron out of many are called quantum numbers. For purpose
of locating an electron, atom is divided into different parts and each part assigned with one quantum number.

Atom	Atom Quantum Numbers		ues	Signifies
Shells/ Energy level/ Orbits (K, L, M, N)	Principle quantum number(n)	1, 2, 3, 4,, K, L, M, N,		Orbit size, Radius Energy
Sub-shells (s, p, d, f)	Azimuthal quantum number ( <i>l</i> )	0, 1, 2, 3, 4 (s) (p) (d) (f) (g)		Angular momentum electron repulsion, finding probability, area (shape)
Sub-subshell (or) orbital $(s, p_x, d_{xy})$	Magnetic quantum number (m)	-l0+l $-40+4$		Orientation
2 electrons with opposite spin	Spin quantum number (s)	+ $\frac{1}{2}$ (clockwise spin)	-\frac{1}{2} (anti-clockwise spin)	Spin

#### **Numerical concept**

Maximum number of electrons in



Number of orbitals in

a orbit = 
$$n^2$$
 a subshell =  $(2l + 1)$ 

Number of subshell in

a orbit = 
$$n$$

Angular

momentum

orbital

 $\frac{h}{2\pi}\sqrt{l(l+1)}$ 
 $\Rightarrow spin \Rightarrow \frac{h}{2\pi}\sqrt{s(s+1)}$ 

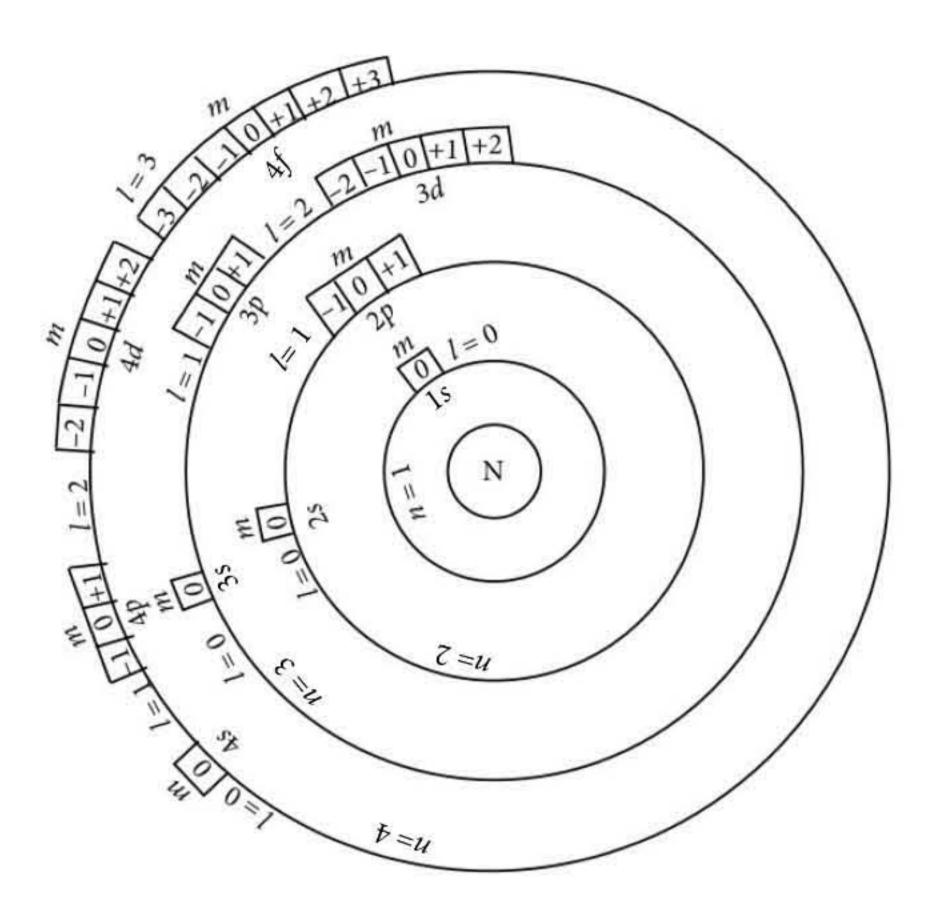
s = Total spin

• Spin multiplication = 2s + 1

	Subshell	1	Orbitals	Electrons
(1)	s	0	1	2
(2)	p	1	3	6
(3)	d	2	5	10
(4)	f	3	7	14
(5)	g	4	9	18

Permitted values :

n	1n
1	0(n-1)
m	-l0+l
s	$+\frac{1}{a}$ and $-\frac{1}{a}$



#### Rules for writing configuration

- **Aufbau's principle :** Subshells are filled with electrons in increasing order of energy. 1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < ......
- Bohr's-Bury rule or (n + l) rule Energy of subshell directly proportional to (n + l) value and if (n + l) is same, then directly proportional to n.

#### Example:

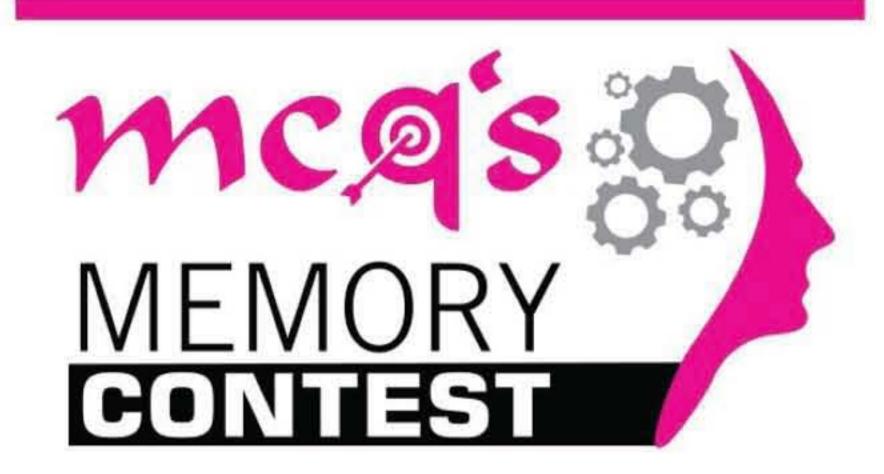
	6 <i>s</i>	5 <i>d</i>	. 60 . 5 .
n+l	6+0=6	5+2=7	$\therefore 6s < 5d$
	5d	6 <i>p</i>	1
n+1	5+2=7	6+1=7	but <i>n</i> of $5d$ is less $\therefore 5d < 6p$

- Pauli's exclusion principle: No. two electrons can have all same set of quantum numbers (or) any orbital can accommodate 2 electrons with antiparallel spin.
- Hund's rule of maximum multiplicity: In degenerate orbitals, all orbitals are singly occupied with electrons before pairing up.

#### **QUESTIONS FOR PRACTICE**

#### **Single Option Correct Type**

- 1. Maximum number of electrons that can be accommodated in a *d*-orbital is
- (a) 10
- (b) 6
- (c) 2
- (d) 14
- 2. Maximum number of possible electrons in  $_{24}$ Cr with s = +1/2, is
- (a) 24
- (b) 12
- (c) 15
- (d) 18





#### Who can participate

If you have taken any of the exams given below and possess plenty of grey cells, photographic memory then you are the right candidate for this contest. All you have to do is write down as many questions (with all choices) you can remember, neatly on a paper with name of the exam, your name, address, age, your photograph and mail them to us.



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- Payment will be made only for complete questions.
- Preference will be given to the reader sending the maximum complete and correct questions. Other conditions apply. The decision of the Editor, MTG shall be final and binding.

- Number of electrons in Cl with n + l = 3, is
- (a)
- (b) 8
- (c) 6
- (d) 3
- If spin quantum number can take three values  $-\frac{1}{2}$ , 0,  $+\frac{1}{2}$  capacity of *p*-subshell will be
- (a) 3
- (b) 6
- (c) 12
- (d) 9
- An orbital having four lobes can have following set of four quantum numbers
- (a) n = 3, l = 2, m = -3
- (b) n = 3, l = 2, m = -2
- (c) n = 4, l = 2, m = 4
- (d) n = 4, l = 3, m = -1
- Set of 4 quantum numbers in 19th electron of Fe  $(1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2)$  is
- (a) n = 3, l = 2, m = +2 to -2,  $s = \pm 1/2$
- (b) n = 4, l = 2, m = +2 to -2,  $s = \pm 1/2$
- (c) n = 4, l = 0, m = +2 to -2,  $s = \pm 1/2$
- (d) n = 4, l = 0, m = 0,  $s = \pm 1/2$
- If element *X* has configuration of *K L M N* then 2 8 13 1

number of electrons in a subshell with l = 2, is

- (a) 10
- (b) 6
- (c) 5
- (d) 2
- Orbital angular momentum of electrons in 3s, 3p respectively is
- (a)  $1\hbar$ ,  $3\hbar$  (b)  $0, 5\hbar$  (c)  $3\hbar$ ,  $6\hbar$  (d)  $0, \sqrt{2}\hbar$

- Configuration which violates Aufbau rule and Pauli's exclusion principle
- (a)
- (b)

- (c)
- (d)
- 10. Which electronic level would allow H atom to absorb photon but not emit photon?
- (a) 3s
- (b) 2s
- (c) 1s
- (d) n

#### More than One Option Correct Type

- 11. Number of electrons that can be accommodated in subshells with (n + l) between 3 to 5 are
- (a) 26
- (b) 38
- (c) 31
- (d) 34
- 12. Which series arranged in maximum increasing order of energy of multi-electron atoms?
- (a) 6s, 4f, 5d, 6p (b) 4f, 6s, 5d, 6p
- (c) 4f, 5d, 6p, 7s (d) 4f, 5d, 6s, 6p
- 13. Ground state of Cr can be represented as

- (b)
- (c) Ar

#### **Matrix Match Type**

**14.** Match the following:

	Column-I		Column-II
1.	l values of p, d, s, f subshells respectively	A.	-2, -1, 0, +1, +2
2.	m values in a subshell with $l = 2$	В.	5
3.	Number of values of <i>l</i> for 3 <sup>rd</sup> shell	C.	1, 2, 0, 3
4.	Number of values of $m$ for subshell $l = 2$	D.	3

#### **Integer Answer Type**

- 15. If Aufbau rule is not followed and electrons are filled shell after shell, number of unpaired electrons in Fe is
- **16.** Number of electrons in Cu having  $n \times l = 0$  is

#### **Hints & Solutions**

1. (c) : Don't confuse with d-orbital with d-subshell.

$$= 1 + 1 + 3 + 1 + 3 + 1 + 5 = 15$$

half electrons of an orbit will have +1/2 and remaining half will have -1/2 spin.

3. **(b)**: 
$${}_{17}\text{Cl} = 1s^2 \ 2s^2 \boxed{2p^6 \ 3s^2} \ 3p^5$$
 $n = 1 \quad 2 \quad 2 \quad 3 \quad 3$ 
 $l = 0 \quad 0 \quad 1 \quad 0 \quad 1$ 
 $n + l = 1 \quad 2 \quad 3 \quad 3 \quad 4$ 

- $\therefore$  Number of electrons with n+l=3 are 8.
- (d): Presently each orbital can take 2 electrons since two values of spin quantum number are possible (+1/2 and -1/2) thus, p-subshell contains 6 electrons but if values of spin quantum number increases to three then *p*-subshell can fill 9 electrons.

- **5. (b)**: As *d*-orbital have four lobes thus the correct option is (b).
- 6. (d):  $19^{th}$  electrons belong to 4s but not 3d.
- 7. (c): K-2 (1 $s^2$ ), L-8 (2 $s^2$  2 $p^6$ ), M-13 (3 $s^2$  3 $p^6$  3 $d^5$ ), N-1 (4 $s^1$ )

l = 2 corresponds to 3d, it contains 5 electrons.

8. (d): 
$$L = \sqrt{l(l+1)} \frac{h}{2\pi} = \sqrt{l(l+1)} \hbar$$

$$3s \Rightarrow l = 0 \Rightarrow L = \sqrt{0(0+1)} \hbar = 0$$

$$3p \Rightarrow l=1 \Rightarrow L=\sqrt{1(1+1)} \ \hbar = \sqrt{2}\hbar$$

- 9. (c):  $\boxed{1}$   $\rightarrow$  Violates Aufbau principle
- $111111 \rightarrow Violates Pauli's rule.$
- **10.** (c) : 1s, as it is lowest level.

11. (a, c, d): 
$$n + l = 3$$
 to 5

$$n+l=3 \implies 3s+2p=8$$

$$n+l=4 \implies 4s+3p=8$$

$$n+l=5 \implies 5s+4p+3d=18$$

Thus, maximum number of electron that can be

accommodated in subshells with (n + l) between 3 to 5 are 34.

12. (a, c) : As per 
$$n + l$$
 rule.

$$l \text{ values} = 0, 1, 2, 3 .... (n-1)$$
  
(s) (p) (d) (f)

$$m \text{ values} = -l \dots 0 \dots + l$$

and number of m values = 2(l) + 1

**15.** (2): Fe(26): 
$$1s^2 2s^2 2p^6 3s^2 3p^6 3d^8$$

 $\therefore$  Number of unpaired electrons = 2

$$n = \begin{bmatrix} 1s^2 \\ 1 \\ l = \\ n \times l = \end{bmatrix} \begin{bmatrix} 2s^2 \\ 2s^2 \\ 0 \\ 0 \end{bmatrix} \begin{bmatrix} 2p^6 \\ 2s^2 \\ 2p^6 \\ 2s^2 \\ 2p^6 \\ 3s^2 \\ 3p^6 \\ 3s^2 \\ 3p^6 \\ 4s^1 \\ 3d^{10} \\ 4 \\ 3 \\ 0 \\ 0 \end{bmatrix} \begin{bmatrix} 3d^{10} \\ 4s^1 \\ 4s^1 \\ 3d^{10} \\ 4s^1 \\ 4s$$

 $\therefore$  Number of electrons with  $n \times l = 0$  is,

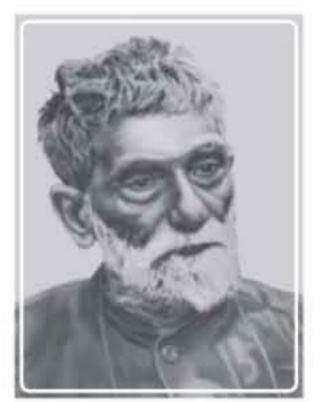
$$= 2 + 2 + 2 + 1 = 7$$

(350)

## Scientist who Made Us Proud

#### **Early Life and Education**

Prafulla Chandra Raychowdhary was born in the village of Raruli-Katipara, which was then situated in the eastern portion of the Bengal Presidency of British He was the third child and son of Harish Chandra Raychowdhury. In 1866, Ray began his education in the village school run by his father, and studied there until he was nine. In 1870 or 1871, when Ray was about 10, his family migrated to the city, where Harish Chandra rented a house at 132 Amherst Street. Ray was admitted to the Hare School the following



Prafulla Chandra Ray (2 August, 1861 – 16 June, 1944)

year. In 1878, he passed the school's Entrance Examination (matriculation exams) with a First Division, and was admitted as an FA (First Arts) student to the Metropolitan Institution.

Though Ray had primarily focused on history and literature until this stage, chemistry was then a compulsory subject in the FA degree. As the Metropolitan Institution offered no facilities for science courses at that time, Ray attended physics and chemistry lectures as an external student at the Presidency College. He was especially drawn to the chemistry courses taught by Alexander Pedler, an inspiring lecturer and experimentalist who was among the earliest research chemists in India. Soon captivated by experimental science, Ray decided to make chemistry his career, as he recognised that his country's future would greatly depend on her progress in science.

He passed the FA exam in 1881 with a second division, and was admitted to the BA (B-course) degree of the University of Calcutta as a chemistry student, with a view towards pursuing higher studies in the field. He sailed for the United Kingdom in August 1882, aged 21.

#### **Research and Contributions**

- Mercurous nitrite: Around 1895 Prafulla Chandra started his work in the field of discovering nitrite chemistry which turned out to be extremely effective. In 1896, he published a paper on preparation of a new stable chemical compound: mercurous nitrite. This work made way for a large number of investigative papers on nitrites and hyponitrites of different metals, and on nitrites of ammonia and organic amines.
- Ammonium and alkylammonium nitrites: Ammonium nitrite synthesis in pure form through double displacement ammonium between chloride and silver nitrite is one of the notable contributions of P C Ray. He proved that the pure ammonium nitrite is indeed stable by bring to pass a lot of experiments and explained that it can be sublimed even at 60 °C without decomposition. He prepared a lot of such compounds by double displacement. After that he worked on mercury alkyl- and mercury alkyl aryl-ammonium nitrites.

#### **Awards and Honours**

- Faraday Gold Medal of the University of Edinburgh (1887)
- Companion of the Order of the Indian Empire (CIE; 1912 Birthday Honours list)
- Knight Bachelor (1919 New Year Honours list)
- Fellow of the Royal Asiatic Society of Bengal
- Fellow of the Chemical Society
- · Honorary Member of the Deutsche Akademie, Munich
- Foundation Fellow of the National Institute of Sciences of India

### CHEMISTRY MUSING

#### **SOLUTION SET 72**

- 1. (b): BeO + C + Cl<sub>2</sub>  $\rightarrow$  BeCl<sub>2</sub> + CO
  (Y)
  BeCl<sub>2</sub> + 2H<sub>2</sub>O  $\rightarrow$  Be(OH)<sub>2</sub> + 2HCl
  (Z)
- 2. (b):  $B_2H_6/THF$  besides reacting at (C = C) also selectively reduces only (—COOH) group to (—CH<sub>2</sub>OH) group in cyclic ester.

$$H_3C$$
 $COOH$ 
 $B_2H_6/THF$ 
 $H_3C$ 
 $CH_2OH$ 
 $H_3C$ 
 $CH_2OH$ 
 $H_3C$ 
 $CH_2OH$ 
 $H_3C$ 
 $CH_2OH$ 
 $CH_2OH$ 

3. (a): meq. of oxalate salt as acid in 30 mL = meq. of NaOH used =  $27 \times 0.12$  meq. of oxalate salt as acid in one litre

$$= \frac{27 \times 0.12 \times 1000}{30}$$
or 
$$\frac{9.15}{\text{M.wt. of salt / } y} \times 1000 = \frac{27 \times 0.12 \times 1000}{30} \dots (i)$$

 $(\because y \text{ is replaceable H-atom } \therefore E_{\text{salt}} = M/y)$ 

Also, meq. of oxalate salt as reductant in 30 mL

= meq. of KMnO<sub>4</sub> used =  $36 \times 0.12$ 

... meq. of oxalate salt as reductant in 1 litre

$$=\frac{36\times0.12\times1000}{30}$$

or 
$$\frac{9.15}{\frac{\text{M.wt.of salt}}{2z}} \times 1000 = \frac{36 \times 0.12 \times 1000}{30}$$
 ...(ii)

$$[\because \left(C_2^{3+}\right)_z \longrightarrow \left(2C^{4+}\right)_z + 2ze^- \therefore E_{\text{salt}} = M/2z]$$

.. By eqs. (i) and (ii), 
$$\frac{y}{2z} = \frac{27}{36}$$

$$\therefore 2y = 3z \qquad ...(iii)$$

Also, total cationic charge = total anionic charge x + y = 2z ...(iv)

By eqs. (iii) and (iv), x : y : z :: 1 : 3 : 2

4. (c): Graham's law of diffusion is applicable to effusion, so we have

$$\frac{r_{\text{mix}}}{r_{\text{Kr}}} = \sqrt{\frac{M_{\text{Kr}}}{M_{\text{mix}}}}$$

or 
$$1.16 = \sqrt{\frac{84}{M_{\text{mix}}}}$$
 or  $1.16 \times 1.16 = \frac{84}{M_{\text{mix}}}$ 

or 
$$M_{mix} = \frac{84}{1.16 \times 1.16}$$
 or 62.42 amu

Now, let the fraction of  $Cl_2$  molecules dissociated at equilibrium = x

$$Cl_2 \iff 2Cl_2$$
Initial 1.0 0
Equi.  $(1-x)$  2x

Total number of moles = (1 + 2x - x) = 1 + x

$$\therefore M_{\text{mix}} = \frac{2x \times M_{\text{Cl}} + (1-x)M_{\text{Cl}_2}}{(1+x)}$$

or 
$$62.42 = \frac{2x \times 35.5 + (1-x)71}{1+x}$$
  
=  $\frac{71x + 71 - 71x}{1+x} = \frac{71}{1+x}$ 

or 
$$(62.42)(1+x)=71$$

or 
$$1+x = \frac{71}{62.42} = 1.137$$
 or  $x = 0.137$ 

5. (c): At boiling point,  $P'_M = 740.2 \text{ mm}$ 

 $P'_{\rm H_2O} = 530.1 \,\rm mm$ 

$$P'_{\text{chlorobenzene}} = 740.2 - 530.1 = 210.1 \text{ mm}$$
Also,  $P'_{\text{H}_2\text{O}} = P'_M \times \text{mole fraction of H}_2\text{O}$ 

 $530.1 = 740.2 \times \text{mole fraction of H}_2\text{O}$ 

 $\therefore$  mole fraction of H<sub>2</sub>O = 0.716

 $\therefore$  mole fraction of  $C_6H_5Cl = 0.284$ 

Let a g  $H_2O$  and b g chlorobenzene be present in distillate.

or 
$$\frac{a/18}{\frac{b}{112.5} + \frac{a}{18}} = 0.716$$
 ...(i)

and 
$$\frac{b/112.5}{\frac{b}{112.5} + \frac{a}{18}} = 0.284$$
 ...(ii)

By eqs. (i)/(ii)
$$\frac{a}{18} \times \frac{112.5}{b} = \frac{0.716}{0.284} \text{ or } \frac{a}{b} = \frac{12.89}{31.95} = 0.403 \quad \dots \text{(iii)}$$
Let total amount of distillate be 100 g, than  $a+b=100 \qquad \qquad \dots \text{(iv)}$ 
By eqs. (iii) and (iv)  $a=28.73 \text{ g}$ 

$$b=71.27 \text{ g}$$
6. (b):  $(K^+ + NH_4^+)$ 

$$\text{Mixture of two cations } (A) \qquad (B) \qquad \text{KClO}_4 \downarrow + NH_4^+$$

$$\text{White ppt. (C)}$$

$$\text{Cations } (A) \qquad (B) \qquad \text{NaOH}$$

$$\text{HgO.Hg } (NH_2)\text{I} \qquad \text{KOH} \qquad NH_3 \uparrow$$

$$\text{(Brown ppt.)} \qquad \text{NH}_3 \uparrow$$
7. (d):

Et
$$\text{Claisen condensation} \qquad \text{Claisen condensation}$$

$$\text{Source of carbanion} \qquad \text{Et}$$

$$\text{O} \qquad \text{Condensation} \qquad \text{CH} \rightarrow \text{CH} \rightarrow \text{CH} \rightarrow \text{CH}$$

$$\text{CH} = \text{O} \qquad \text{H} \rightarrow \text{CH} \rightarrow \text{CH} \rightarrow \text{CH}$$

$$\text{CH} = \text{O} \qquad \text{H} \rightarrow \text{CH} \rightarrow \text{CH} \rightarrow \text{CH}$$

$$\text{CH} = \text{O} \qquad \text{H} \rightarrow \text{CH} \rightarrow \text{CH} \rightarrow \text{CH}$$

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$$\text{CH} = \text{O} \qquad \text{CH} \rightarrow \text{CH}$$

$$\text{CH} \rightarrow \text{CH}$$

$$\text{CH} \rightarrow \text{CH} \rightarrow \text{CH}$$

$$\text{CH} \rightarrow \text{CH}$$

 $(\alpha, \beta$ -Unsaturated ketone)

10. (2.424) :  $_{+1}e^0 +_{-1}e^0 \to 2\gamma$  (photons of same energy)

The energy produced during emission of two photons =  $2 \times m_e \times c^2$ 

=  $2 \times 9.109 \times 10^{-31} \times (3.0 \times 10^{8})^{2} = 163.96 \times 10^{-15} \text{ J}$ Energy produced per photon

$$= \frac{16.396 \times 10^{-14} \text{J}}{2} = 8.198 \times 10^{-14} \text{J}$$

Using Einstein equation,

 $E = \frac{hc}{\lambda}$ , where c = velocity of light,  $\lambda =$  wavelength of particle

$$\therefore 8.198 \times 10^{-14} = \frac{6.625 \times 10^{-34} \times 3.0 \times 10^{8}}{\lambda}$$

$$\lambda = \frac{6.625 \times 10^{-34} \times 3.0 \times 10^{8}}{8.198 \times 10^{-14}} = 2.424 \times 10^{-12} \text{m}$$

$$\lambda = 2.424 \text{ pm}$$

## CHEMISTRY PUZZLE SOLUTION JULY 2019

MAGNESIUM CREATININE **ACETOMINOPHEN GLUCOSE** CALCIUM **AMYLASE CHOLESTEROL PHOSPHORUS** LIPASE **CHLORIDE** POTASSIUM CARBONATE SODIUM **ALCOHOL BLOODGAS ALBUMIN** LACTATE BILIRUBIN



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